DP-MS-86-11

TRITIUM SEPARATION USING METAL HYDRIDES

by

M. W. Lee

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

A paper proposed for presentation at the
Gordon Research Conferences
Oxnard, CA
February 10-14, 1986

This document was prepared in conjunction with work accomplished under Contract No.
DE-AC09-76SR00001 with the U.S. Department of Energy.

DP-MS-86-11

TRITIUM SEPARATION USING METAL HYDRIDES*

by

M. W. Lee

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29808

ABSTRACT

1. **Metal Hydrides**

   Characteristics
   Properties
   Applications

2. **Isotope Effects**

   Separation Factors
   Model Calculations

3. **Separation Technique**

   Chromatograph
   Thermal Cycling Absorption Process (TCAP)

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

Some of the metal hydride and intermetallic compounds readily absorb the hydrogen gas by a simple contact to form metal hydrides. Metal hydrides have several important properties for the hydrogen isotope separation:

- Reversibly absorb and desorb.
- Hold large quantities of the hydrogen gas.
- Have large isotope effect.
- Hold the hydrogen gas as loosely-bound atomic hydrogen. Several applications for the metal hydrides are storage, compressor, and isotope separation.

Metal Hydride

$M + (N/2)\ H_2 — MH_N$

$PbH_{0-0.07} \cdot UH_{0-3} \cdot LaNi_5\ H_{0-6}$

Properties

- Reversibly absorb/desorb hydrogen gas
- Large quantities of hydrogen in small volume
- Large isotope effect
- Atomic hydrogen desolved in metal

Applications

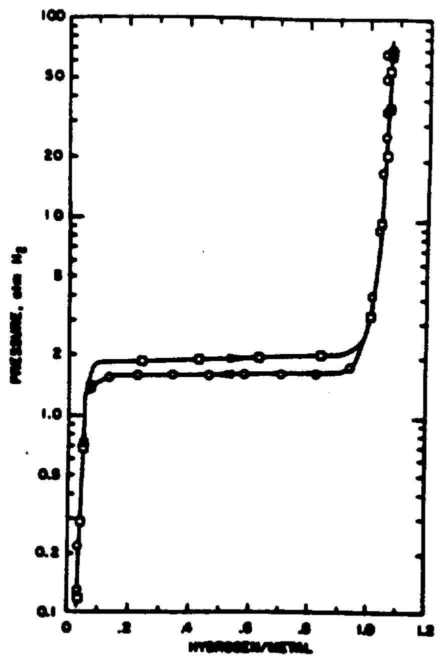
- Storage
- Compressor/pump
- Hydrogen purifier
- Isotope separation

Storage Capability

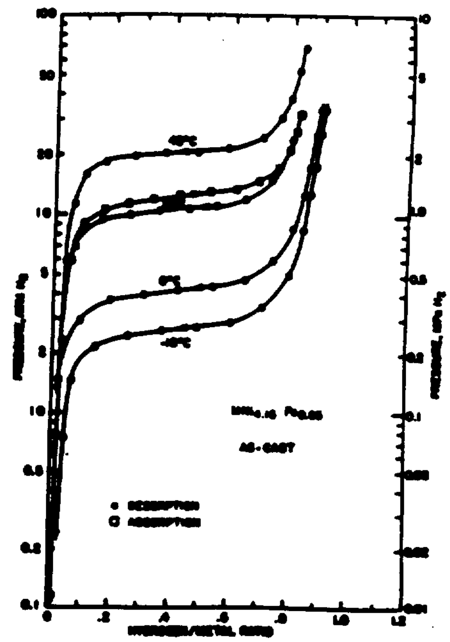
(Liquid hydrogen at 20 k	35 moles/liter)
(Water	56 moles/liter)
$P_D\ H_{0.7}$	37 moles/liter)
$U\ H_3$	120 moles/liter)
$LaNi_5H_6$	59 moles/liter)

Metal hydride can hold more hydrogen in a given volume than liquid hydrogen. Therefore, the isotope separation using metal hydride is a high density operation.

ISOTHERM



ABSORPTION AND DESORPTION ISOTHERMS FOR $LaNi_5$ AT 20°C.



STATIC HYDROGEN ABSORPTION/DESORPTION ISOTHERMS FOR ($MmNi_{4.15}Fe_{0.85}$)

Typical isotherms are shown on this slide. As metal absorbs the hydrogen gas, the equiliblium overpressure increases until it reaches a plateau where metal hydride absorbs the hydrogen gas with little change of the equiliblium pressure.

When metal hydride become near saturation, the equiliblium pressure increases exponentially. The desorption plateau is lower than absorption plateau because of hysteresis which occur during the phase change from alpha to beta phases.

The plateau pressure increases as the temperature increases.

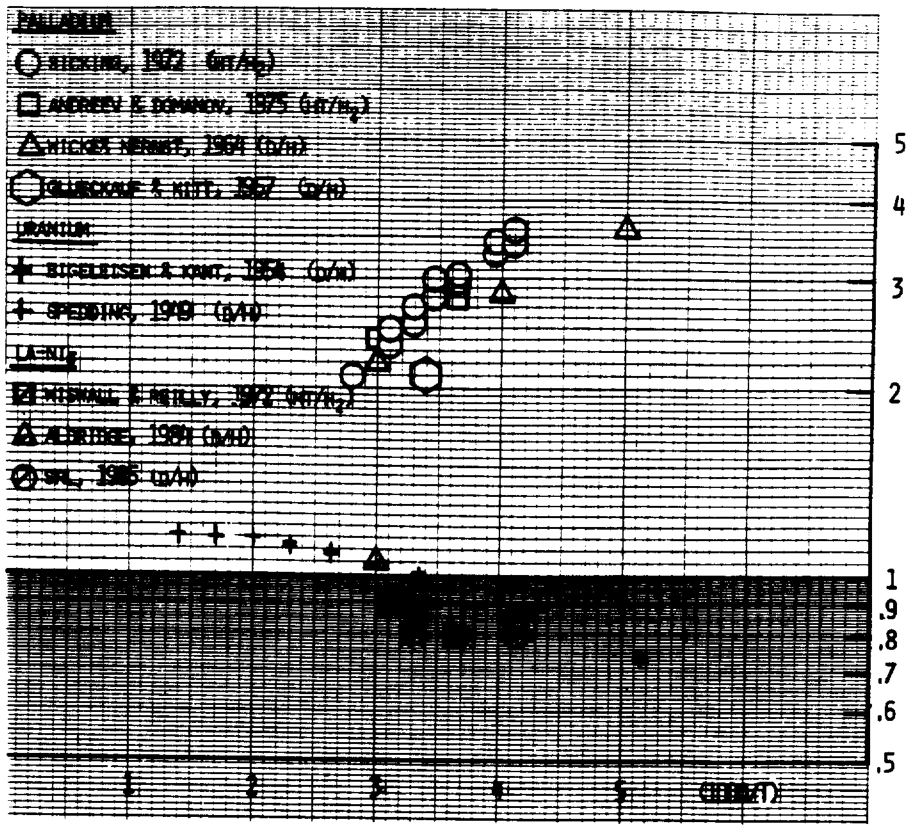
SEPARATION FACTOR

DEFINITION

$$\alpha = \frac{(D/H)_{GAS}}{(D/H)_{SOLID}} = \frac{(T/H)_{GAS}}{(T/H)_{SOLID}} = \frac{(T/D)_{GAS}}{(T/D)_{SOLID}}$$

The separation factor is defined by the isotopic ratio in the gas phase to that in the solid phase.

SEPARATION FACTOR



The separation factors of palladium, uranium and LaNi5 have been reported. I like to point out two important observations: 1) palladium has large separation factors even near room temperature; 2) palladium has a positive slope to the inverse of the temperature. but uranium and LaNi5 have negative slopes.

SEPARATION FACTOR (MODEL)

GAS PHASE PARTITION FUNCTION RATIO

J. BRON, C.F. CHANG, AND M. WOLFSBERG

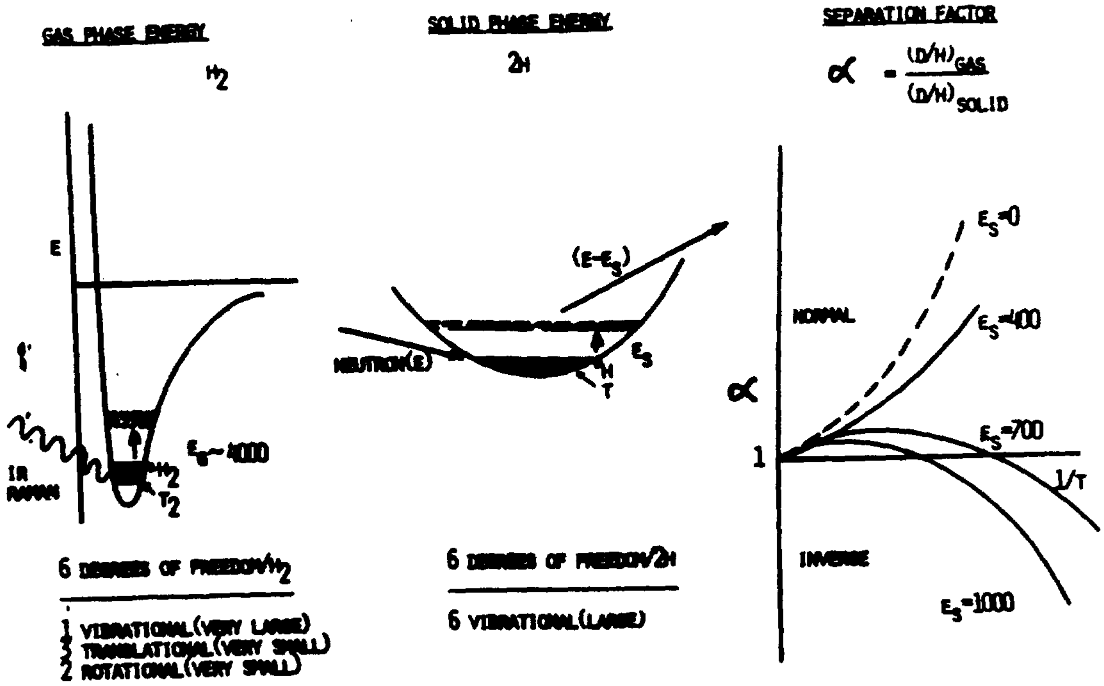
Z. NATURFORSCH 28 A, 129 (1974)

SOLID PHASE PARTITION FUNCTION RATIO

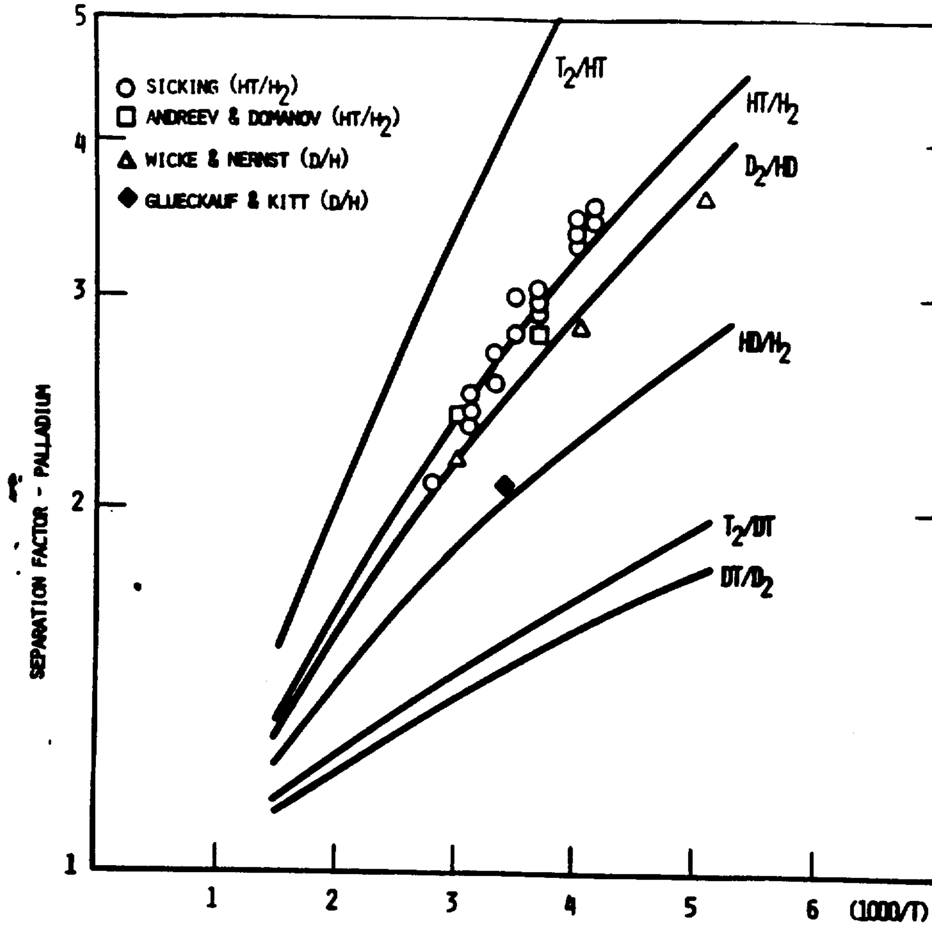
- ATOMIC HYDROGEN TRAPPED IN A POTENTIAL WELL
- 3 DIMENSIONAL OSCILLATOR : HARMONIC/ANHARMONIC
- FUNDAMENTAL FREQUENCIES OBSERVED BY INELASTIC NEUTRON SCATTERING (OVERTONE AND ISOTOPIC FREQUENCIES)

To calculate the separation factors, I used the gas phase partition fuction of Bron, Chang, and Wolfsberg in 1974. To calculate the solid phase partition fuction ratio, I assume following:

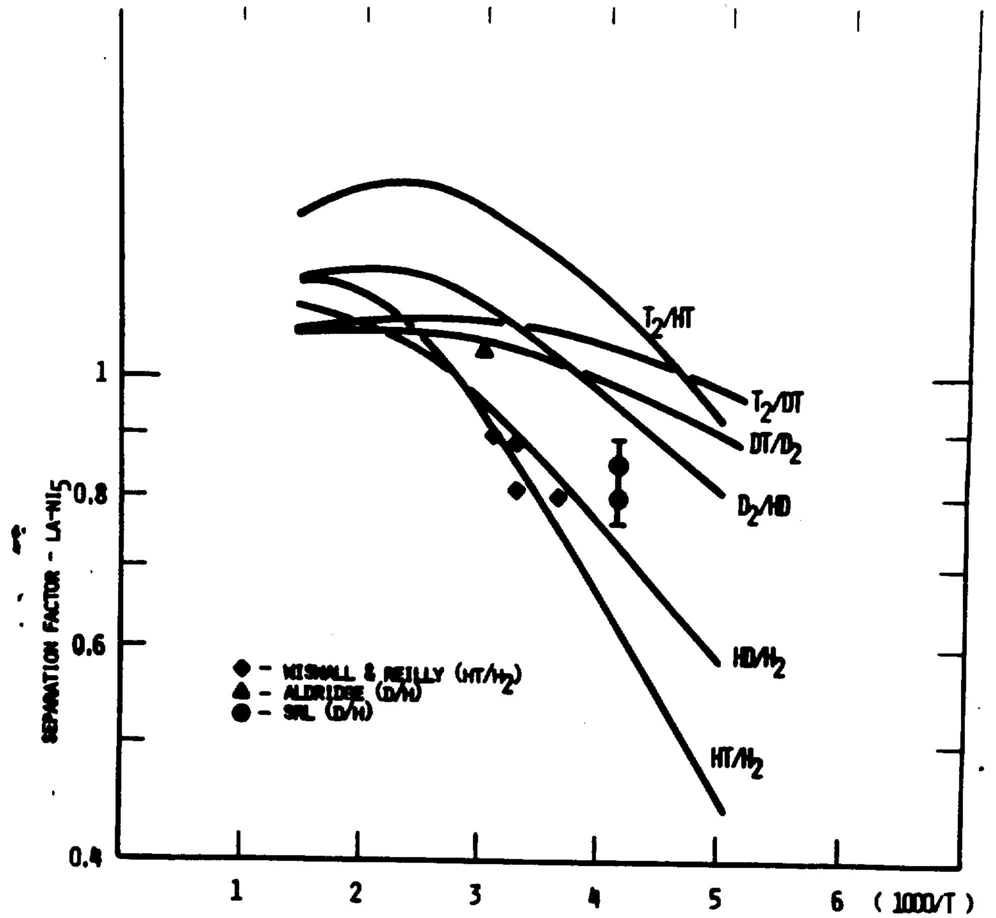
1) Atomic hydrogen is trapped in a potential well provided by the solid.
2) Each atom is a three dimensional oscillator.
3) The fundamental frequencies are measured by an inelastic neutron scattering.



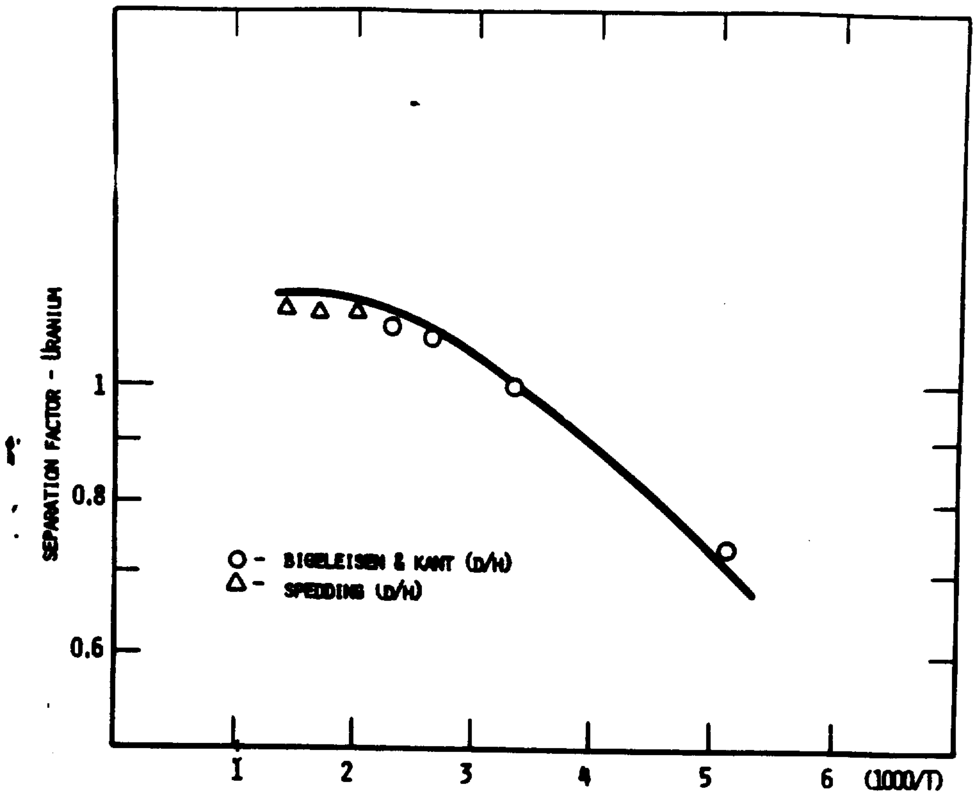
In the gas phase, one vibrational frequency contribute the most to the partition fuction ratio. In the solid phase, six vibrational frequencies per two atoms contribute to the partion fuction ratio. By increaseing the fundamental frequency of the atom, the separation factor systematically shifts and the cross-over phenomena occurs near 700 wave number.



Palladium has large separation factors. This is the best candidate for the isotope separation. The concentration dependence is also shown here. For example, the low concentration of tritium follows HT/H2 curve while the high concentration of tritium follows T2/HT curve. All other falles in between.



The results of LaNi5 are shown in this slide.



The results of uranium are shown in this slide.

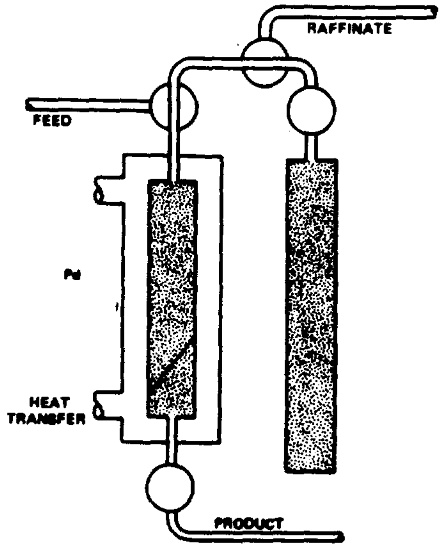
SEPARATION TECHNIQUE

CHROMATOGRAPH

THERMAL CYCLING ABSORPTION PROCESS
(TCAP)

Chromatographic technique has been used to separate the hydrogen isotopes. What I like to discuss with you today is a new technology developed by Savannah River Laboratory. It is a continuous chromatographic method.

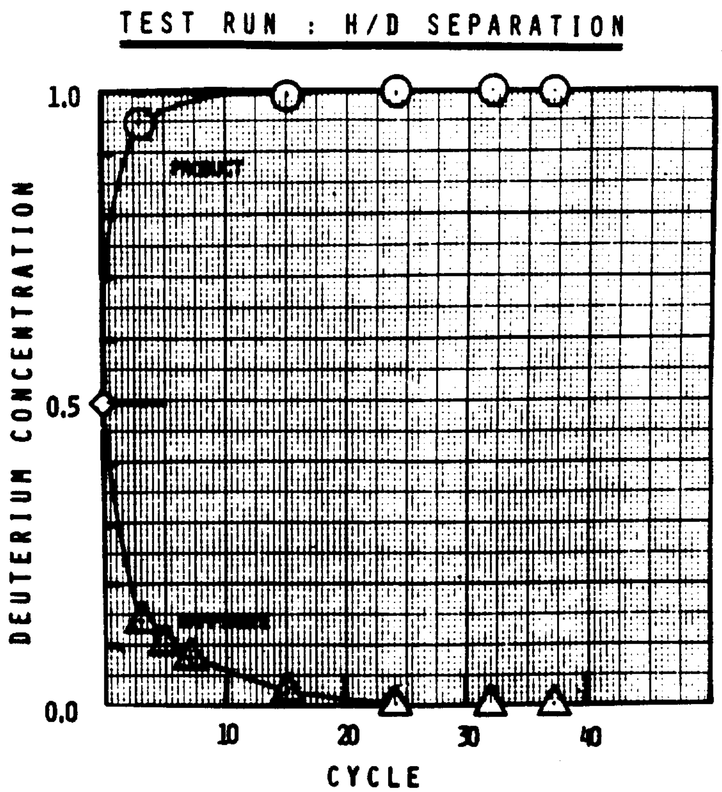
THERMAL CYCLING ABSORPTION PROCESS (TCAP)



A concept is shown in this slide. The TCAP has two columns interconnected. One column is packed with palladium and the other a neutral (no metal hydride).

During the heating/cooling cycles, the hydrogen gas moves back and forth between two columns. During the absorption at low temperature, the heavier isotope is enriched at the bottom of the palladium column and depreted at the top of the column.

After about 20 cycles, it reaches a steady state and forms a sharp boundary. At this point, the mixture is fed and the product and raffinate are drawn off from the column.



The test run for H/D separation is shown in this slide.

TRITIUM SEPARATION USING METAL HYDRIDES

MYUNG W. LEE

SAVANNAH RIVER LABORATORY

E. I. DU PONT DE NEMOURS & CO.

SPONSOR: U.S. DEPARTMENT OF ENERGY

CONTRIBUTORS:

M. W. LEE
G. S. NICHOLS
W. N. POSEY
L. K. HEUNG
M. S. ORTMAN

OVERVIEW

1. METAL HYDRIDES

- CHARACTERISTICS
- PROPERTIES
- APPLICATIONS

2. ISOTOPE EFFECTS

- SEPARATION FACTORS
- MODEL CALCULATIONS

3. SEPARATION TECHNIQUE

- CHROMATOGRAPH
- THERMAL CYCLING ABSORPTION PROCESS (TCAP)

METAL HYDRIDE

$$M + (N/2)H_2 \rightleftharpoons MH_N$$

$PdH_{0\text{-}0.7}$, $UH_{0\text{-}3}$, $LaNi_5H_{0\text{-}6}$

PROPERTIES

- REVERSIBLY ABSOB/DESORB HYDROGEN GAS
- LARGE QUANTITIES OF HYDROGEN IN SMALL VOLUME
- LARGE ISOTOPE EFFECT
- ATOMIC HYDROGEN DESOLVED IN METAL

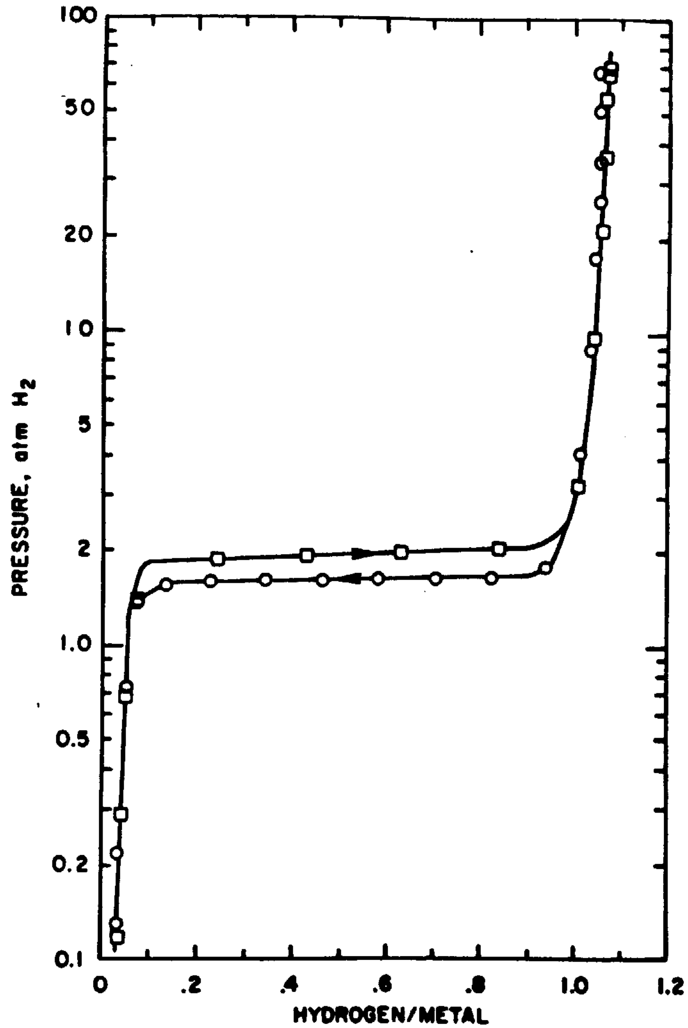
APPLICATIONS

- STORAGE
- COMPRESSOR / PUMP
- HYDROGEN PURIFIER
- ISOTOPE SEPARATION

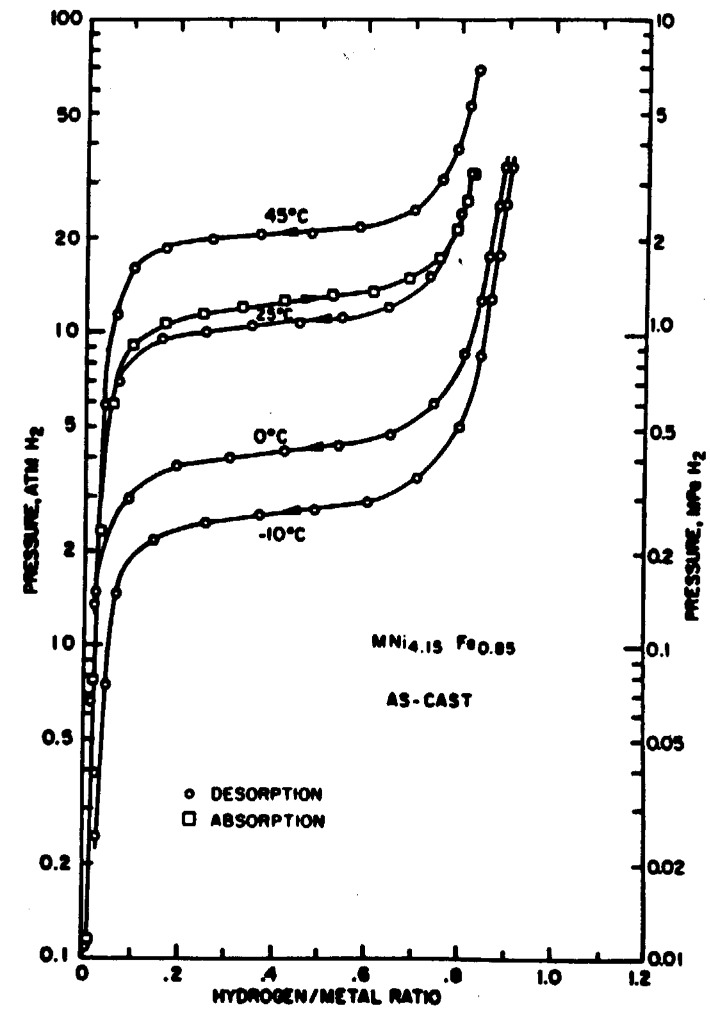
STORAGE CAPACITY

(LIQUID HYDROGEN AT 20K	35	MOLES/LITER)
(WATER	56	")
$PdH_{0.7}$	37	"
UH_3	120	"
$LaNi_5H_6$	59	"

ISOTHERM



ABSORPTION AND DESORPTION ISOTHERMS FOR $LaNi_5$ AT 25°C.



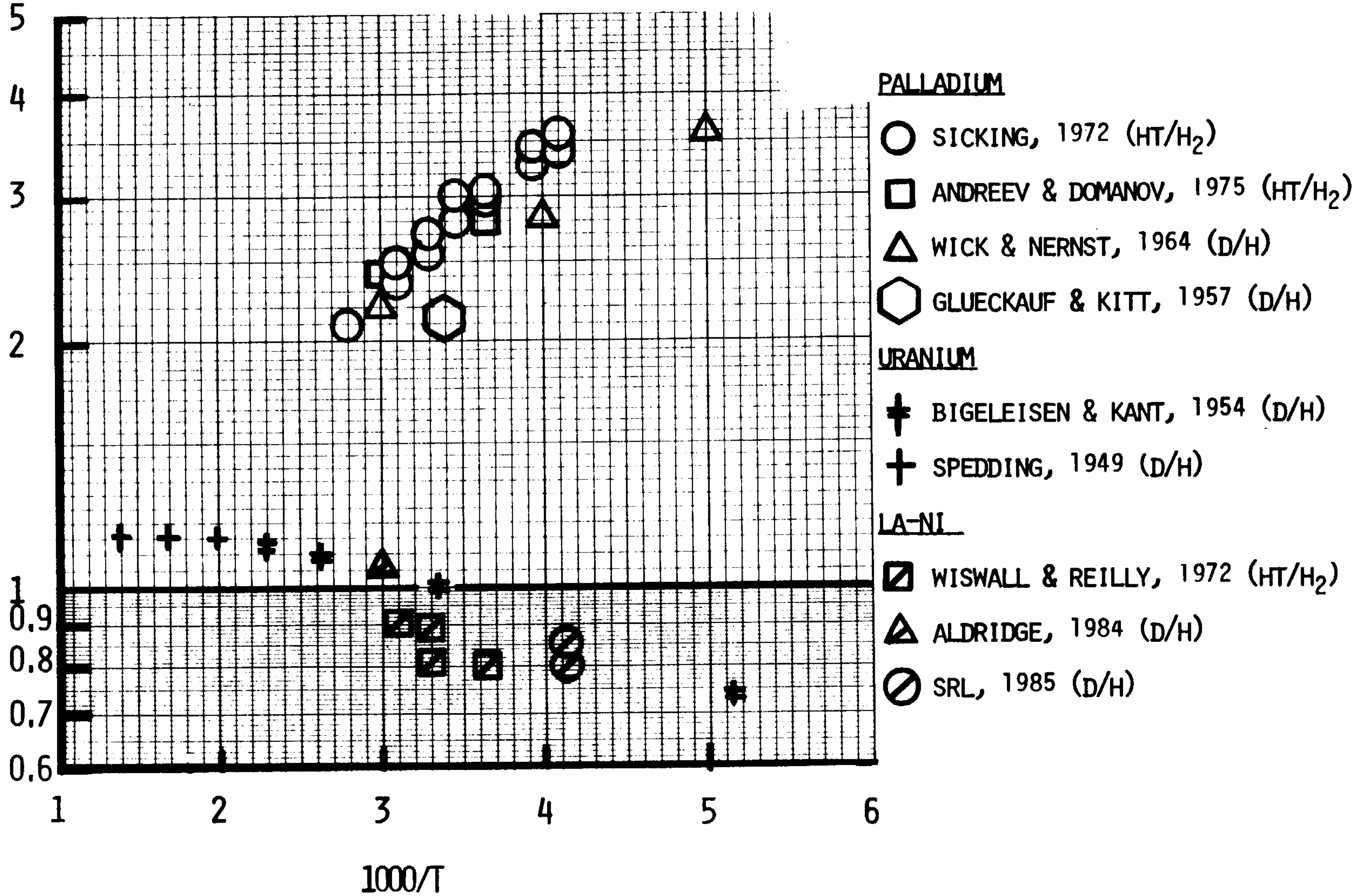
STATIC HYDROGEN ABSORPTION/DESORPTION ISOTHERMS FOR ($MNi_{4.15}Fe_{0.85}$)

SEPARATION FACTOR

DEFINITION

$$\alpha = \frac{(D/H)_{GAS}}{(D/H)_{SOLID}} = \frac{(T/H)_{GAS}}{(T/H)_{SOLID}} = \frac{(T/D)_{GAS}}{(T/D)_{SOLID}}$$

SEPARATION FACTOR



SEPARATION FACTOR (MODEL)

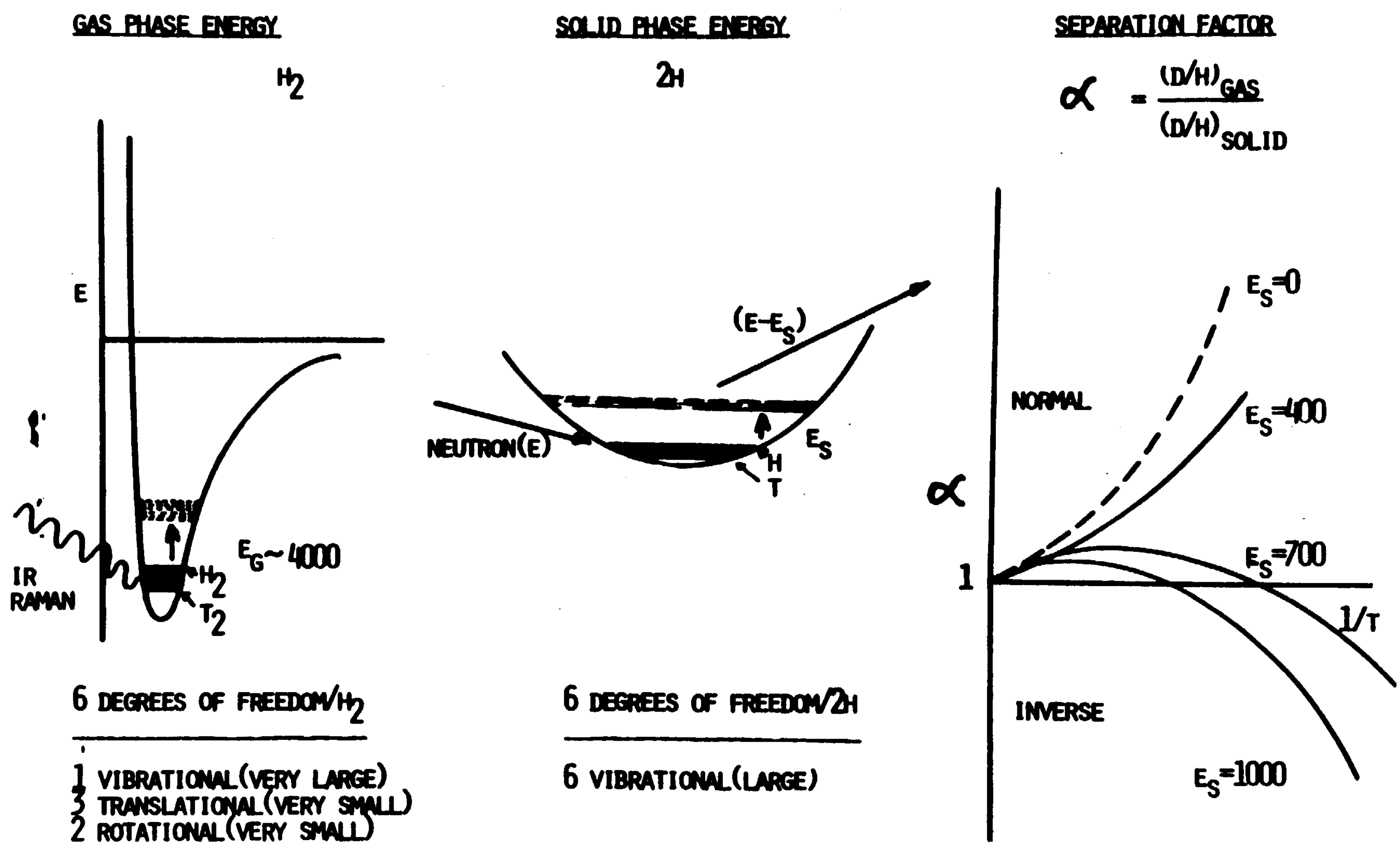
GAS PHASE PARTITION FUNCTION RATIO

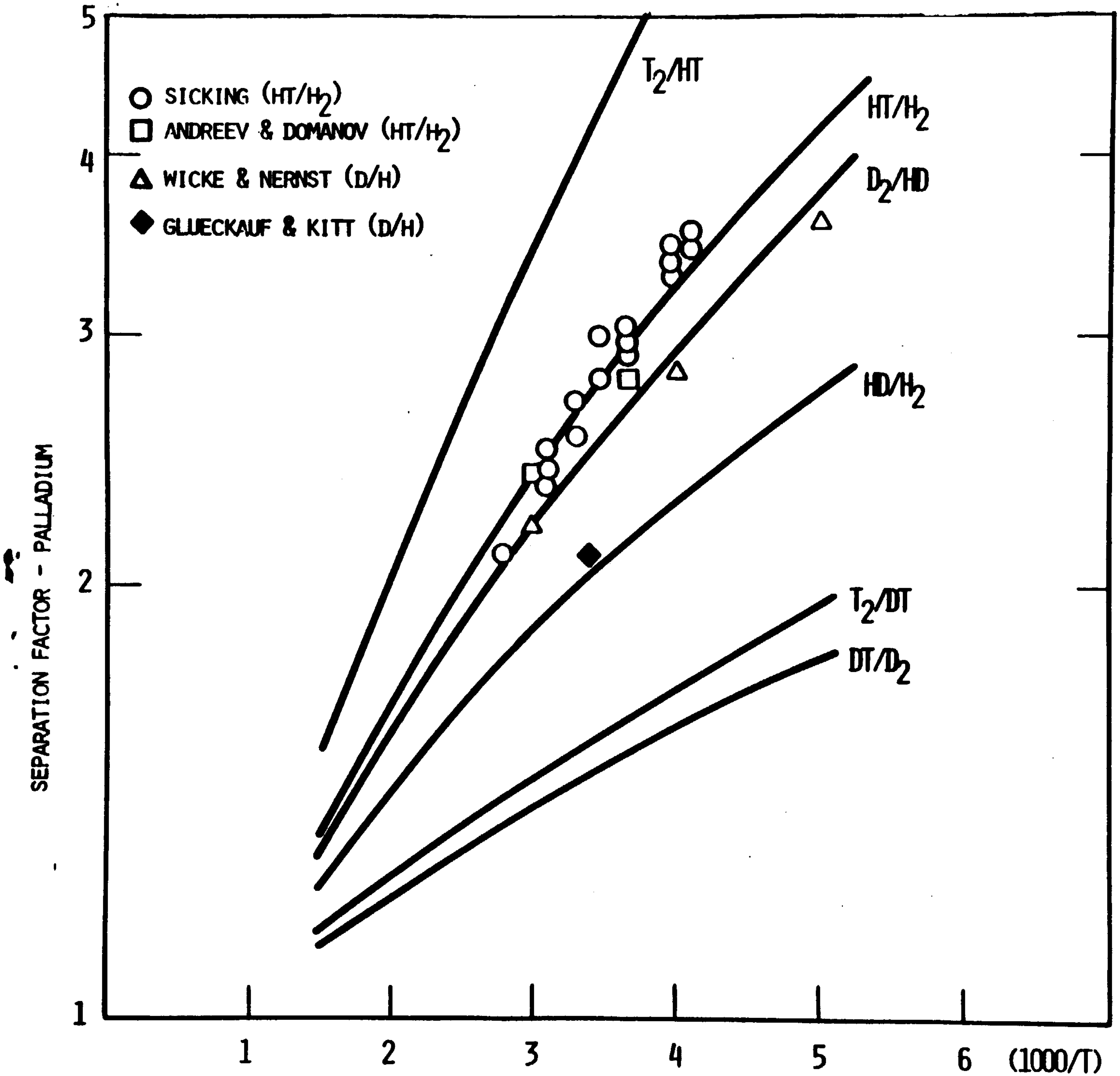
J. BRON, C.F. CHANG, AND M. WOLFSBERG

Z. NATURFORSCH 28 A, 129 (1974)

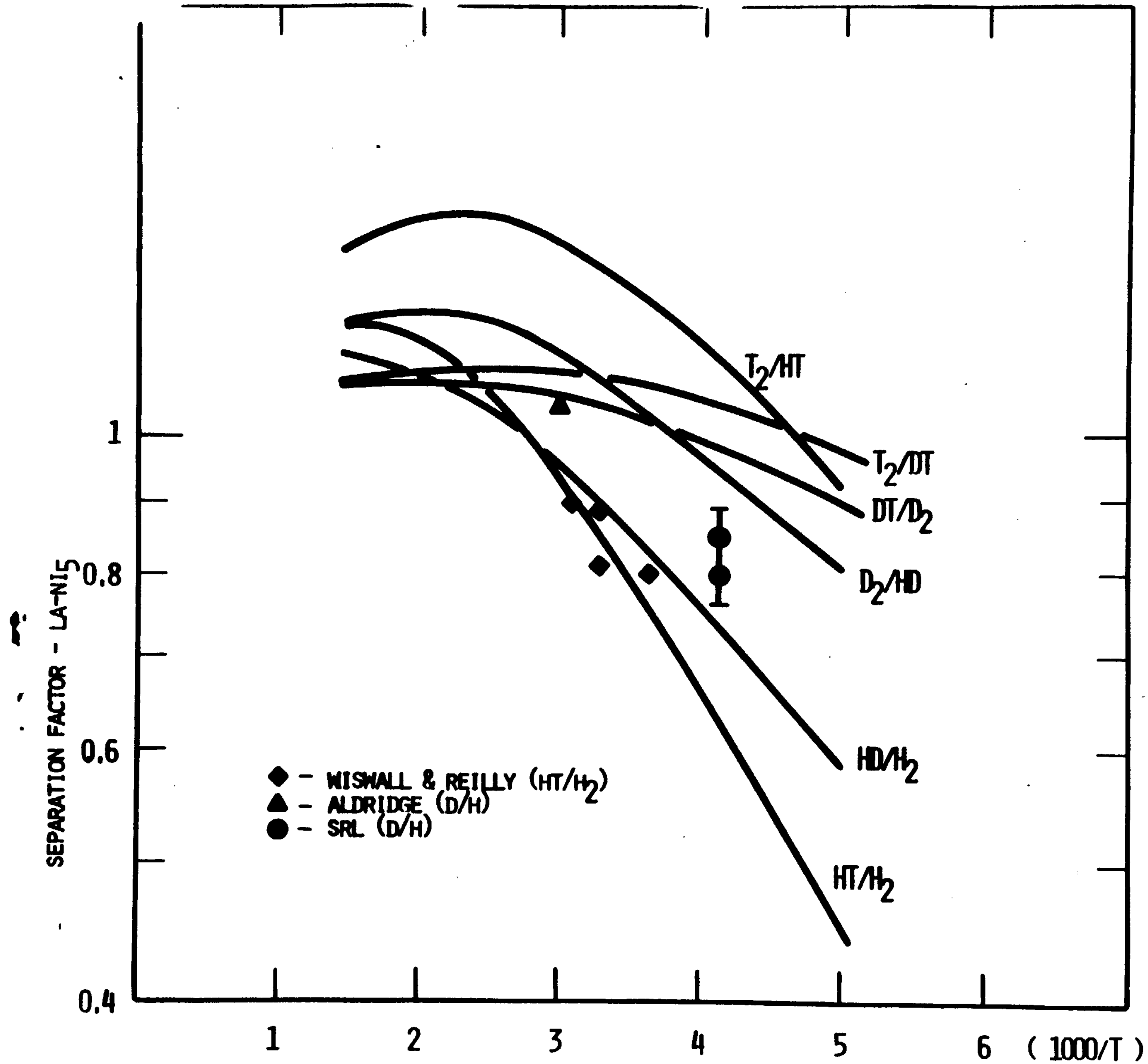
SOLID PHASE PARTITION FUNCTION RATIO

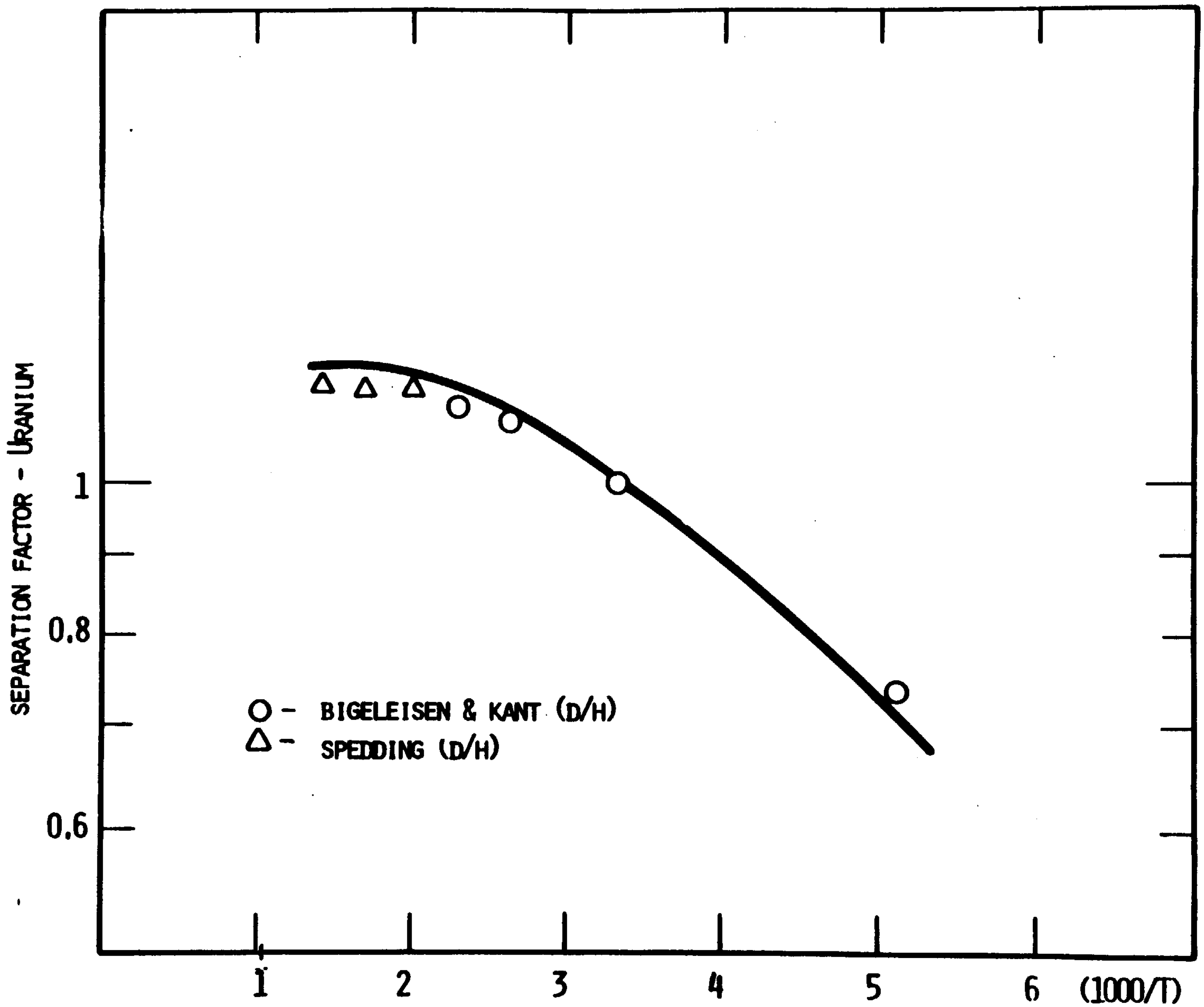
- ATOMIC HYDROGEN TRAPPED IN A POTENTIAL WELL
- 3 DIMENSIONAL OSCILLATOR : HARMONIC/ANHARMONIC
- FUNDAMENTAL FREQUENCIES OBSERVED BY INELASTIC NEUTRON SCATTERING (OVERTONE AND ISOTOPIC FREQUENCIES)


GAS PHASE ENERGY
H2
E
IR
RAMAN
H2
T2
EG~4000
6 DEGREES OF FREEDOM/H2
1 VIBRATIONAL(VERY LARGE)
3 TRANSLATIONAL(VERY SMALL)
2 ROTATIONAL(VERY SMALL)
SOLID PHASE ENERGY
2H
(E-ES)
NEUTRON(E)
ES
H
T
6 DEGREES OF FREEDOM/2H
6 VIBRATIONAL(LARGE)
SEPARATION FACTOR
α = (D/H)GAS / (D/H)SOLID
α
1
NORMAL
INVERSE
ES=0
ES=400
ES=700
ES=1000
1/T



SEPARATION FACTOR - PALLADIUM
SICKING (HT/H2)
ANDREEV & DOMANOV (HT/H2)
WICKE & NERNST (D/H)
GLUECKAUF & KITT (D/H)
T2/HT
HT/H2
D2/HD
HD/H2
T2/DT
DT/D2
1
2
3
4
5
1
2
3
4
5
6
(1000/T)


SEPARATION FACTOR - LA-NI5
0.4
0.6
0.8
1
1
2
3
4
5
6
(1000/T)
T2/HT
T2/DT
DT/D2
D2/HD
HD/H2
HT/H2
◆ - WISWALL & REILLY (HT/H2)
▲ - ALDRIDGE (D/H)
● - SRL (D/H)


SEPARATION FACTOR - URANIUM
1
0.8
0.6
1
2
3
4
5
6
(1000/T)
O - BIGELEISEN & KANT (D/H)
Δ - SPEDDING (D/H)

SEPARATION FACTOR FOR MIXED SYSTEM

$$\alpha_{H/D} = \frac{[H]\,R_{HD/HH} + [D]\,R_{HD/HH}\,R_{DD/HD} + [T]\,R_{HD/HH}\,R_{DD/HD}\,R_{DT/DD}}{[H] + [D]\,R_{HD/HH} + [T]\,R_{HT/HH}}$$

$$\alpha_{H/T} = \frac{[H]\,R_{HT/HH} + [D]\,R_{HD/HH}\,R_{DD/HD}\,R_{DT/DD} + [T]\,R_{HT/HH}\,R_{TT/HT}}{[H] + [D]\,R_{HD/HH} + [T]\,R_{HT/HH}}$$

$$\alpha_{D/T} = \alpha_{H/T} / \alpha_{H/D}$$

[H], [D], & [T] : MOLE FRACTIONS IN THE SOLID PHASE

$R_{AB/CD}$: SEPARATION FACTOR FOR SINGLE ATOM SUBSTITUTION

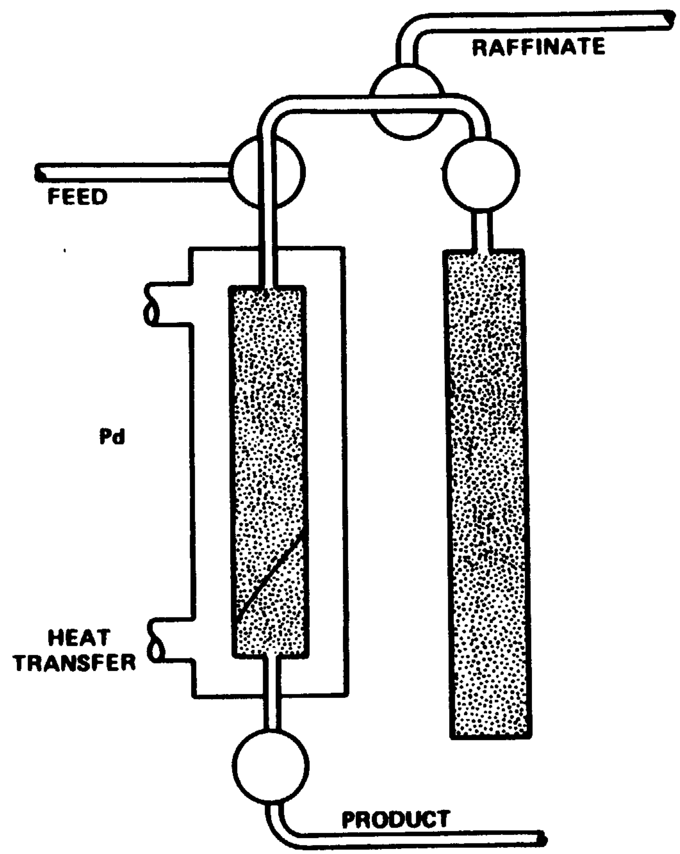
SEPARATION TECHNIQUE

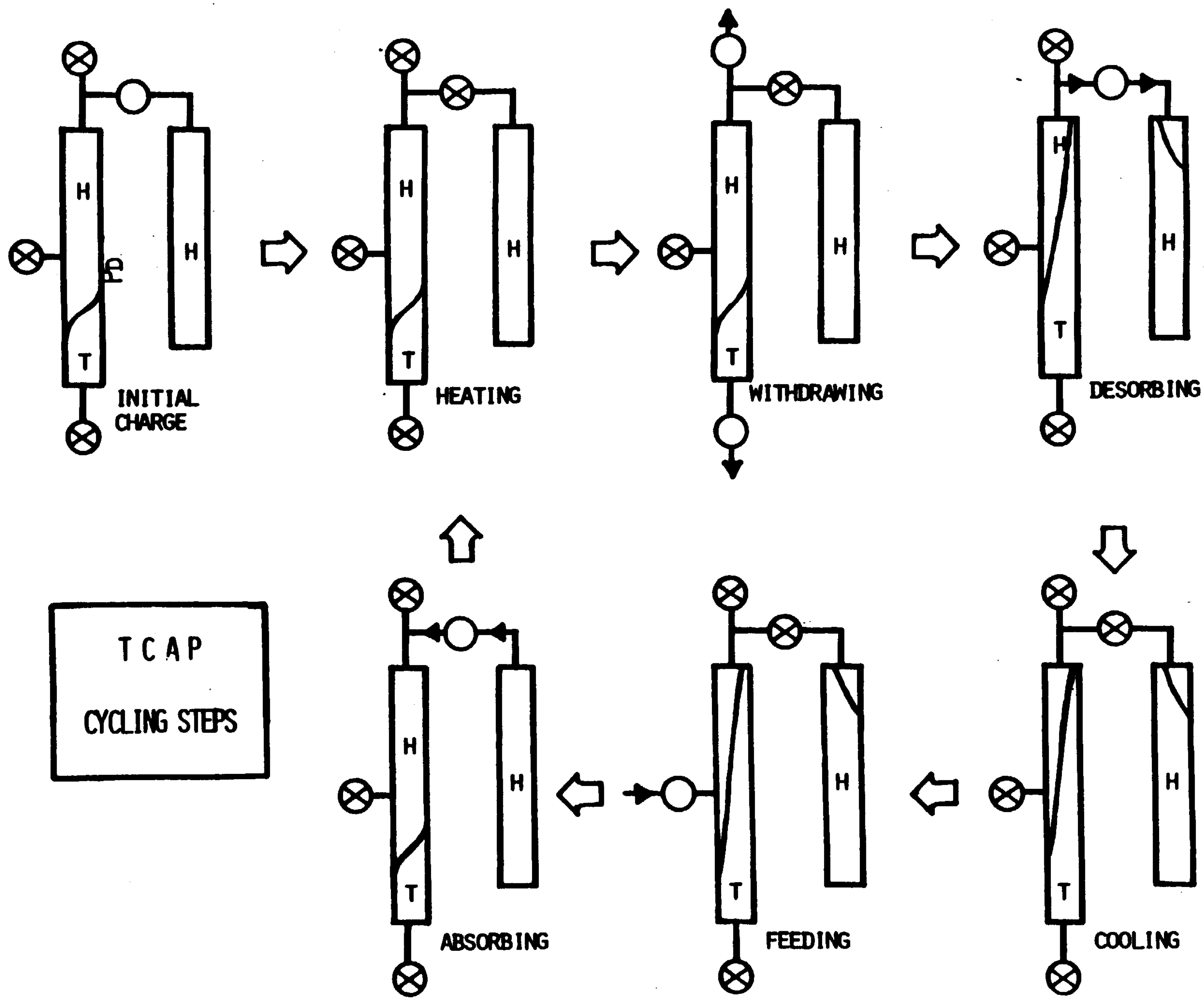
CHROMATOGRAPH

THERMAL CYCLING ABSORPTION PROCESS

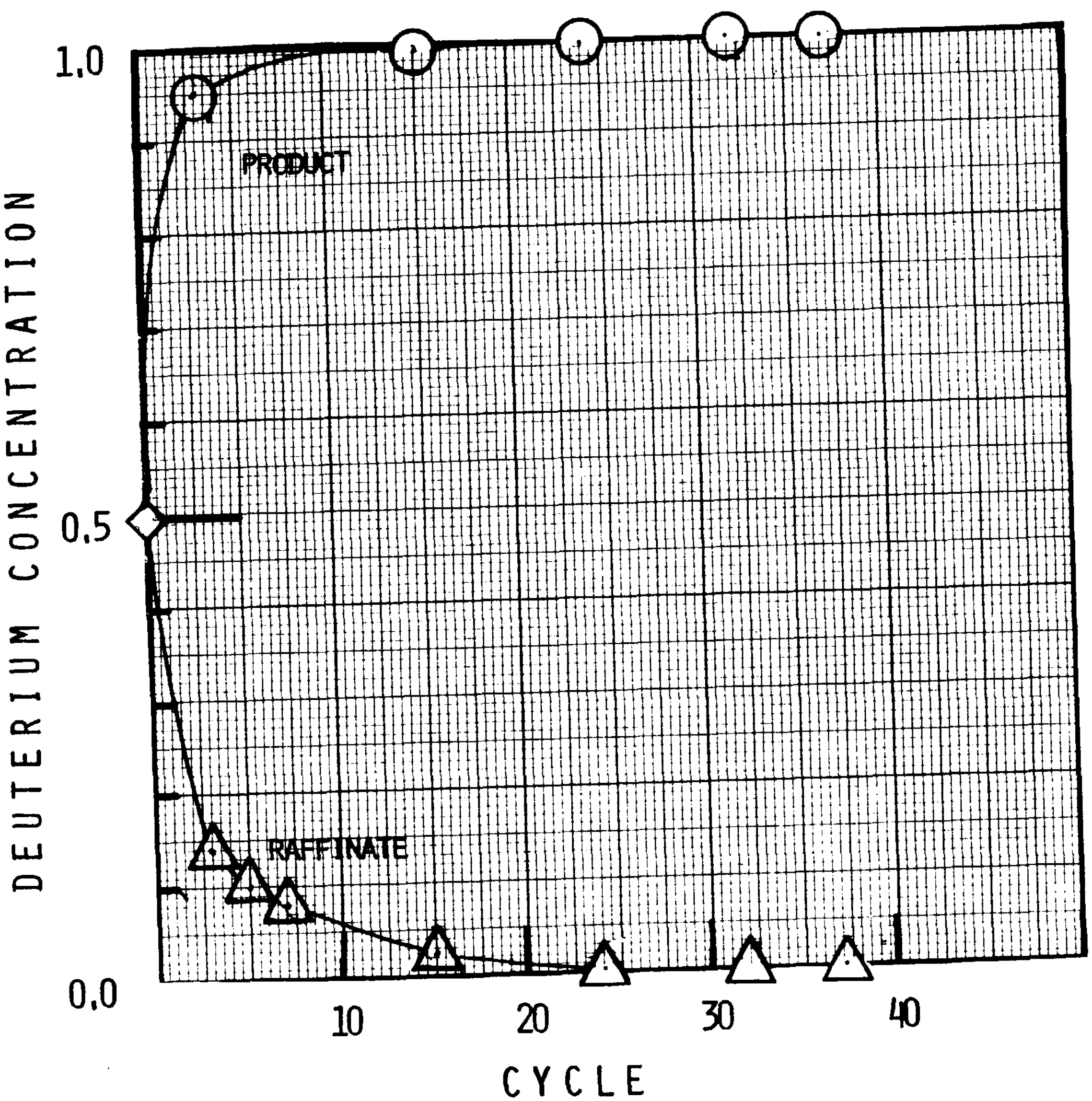
(TCAP)

THERMAL CYCLING ABSORPTION PROCESS (TCAP)




T C A P
CYCLING STEPS
INITIAL CHARGE
PD
HEATING
WITHDRAWING
DESORBING
COOLING
FEEDING
ABSORBING
H
T

TEST RUN : H/D SEPARATION



TCAP vs CURRENT PROCESSES