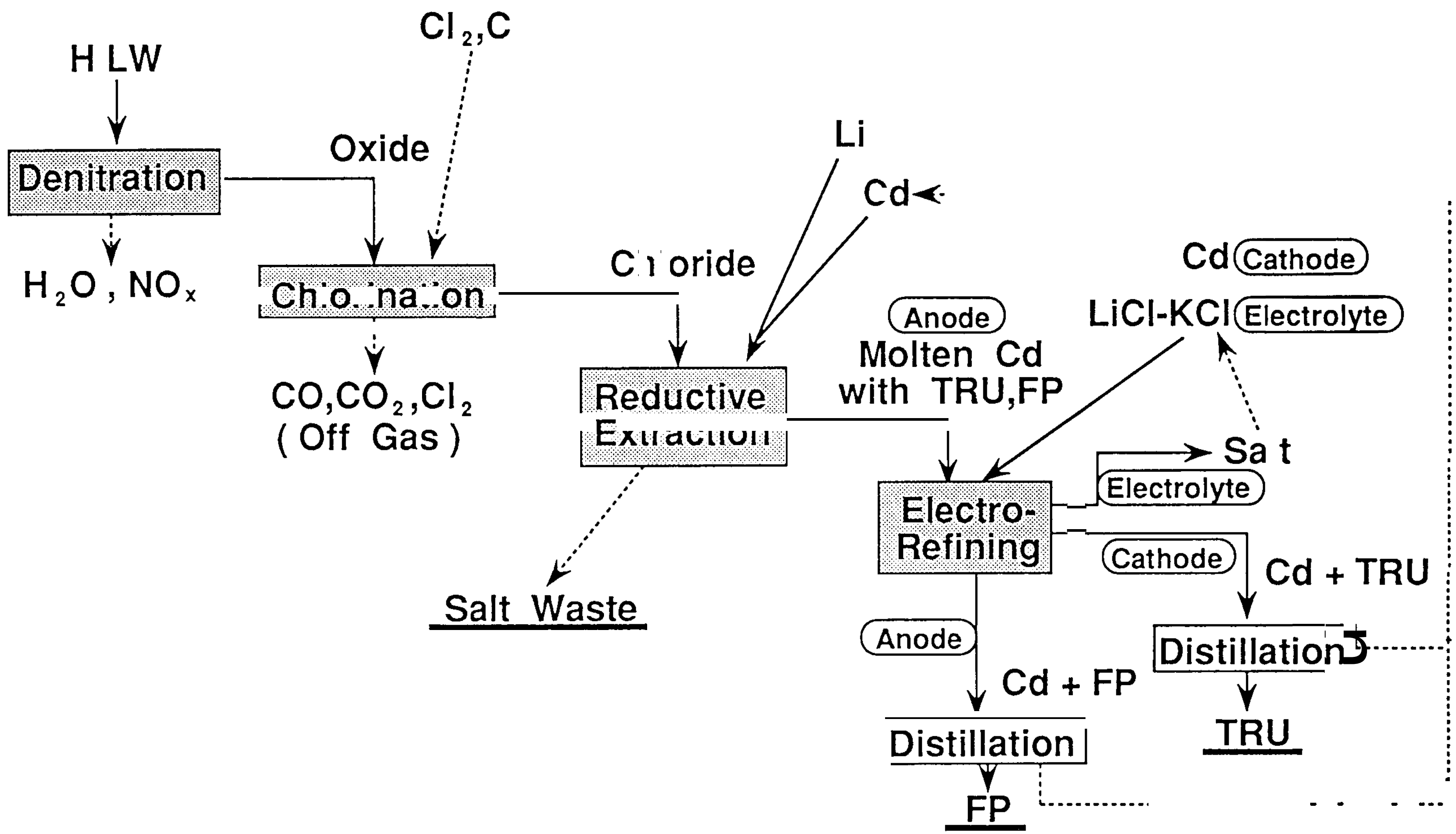
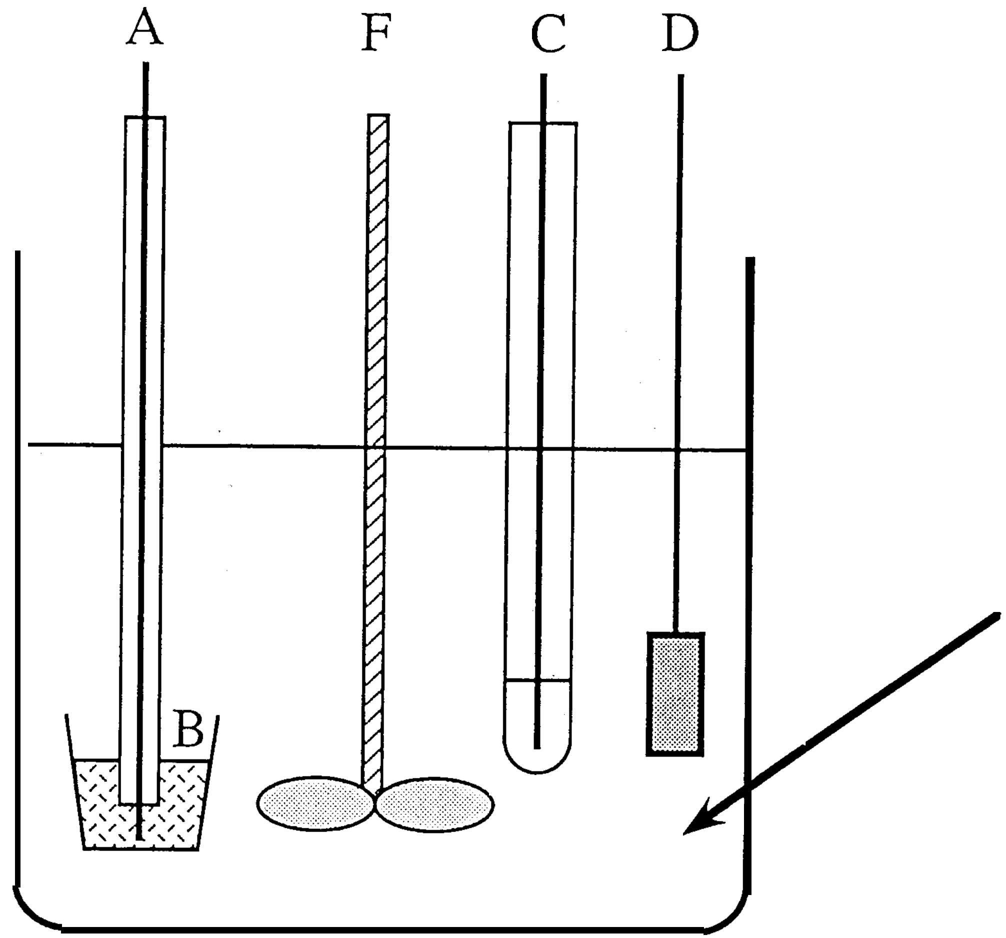
DEVELOPMENT OF PYROMETALLURGICAL PARTITIONING

H. MIYASHIRO, M. SAKATA, T. MATSUMOTO,
T. INOUE, N. TAKAHASHI* and L. GRANTHAM**

Central Research Institute of Electric Power Industry (CRIEPI)
•Kawasaki Heavy Industries, Ltd.
** Rockwell International Corporation

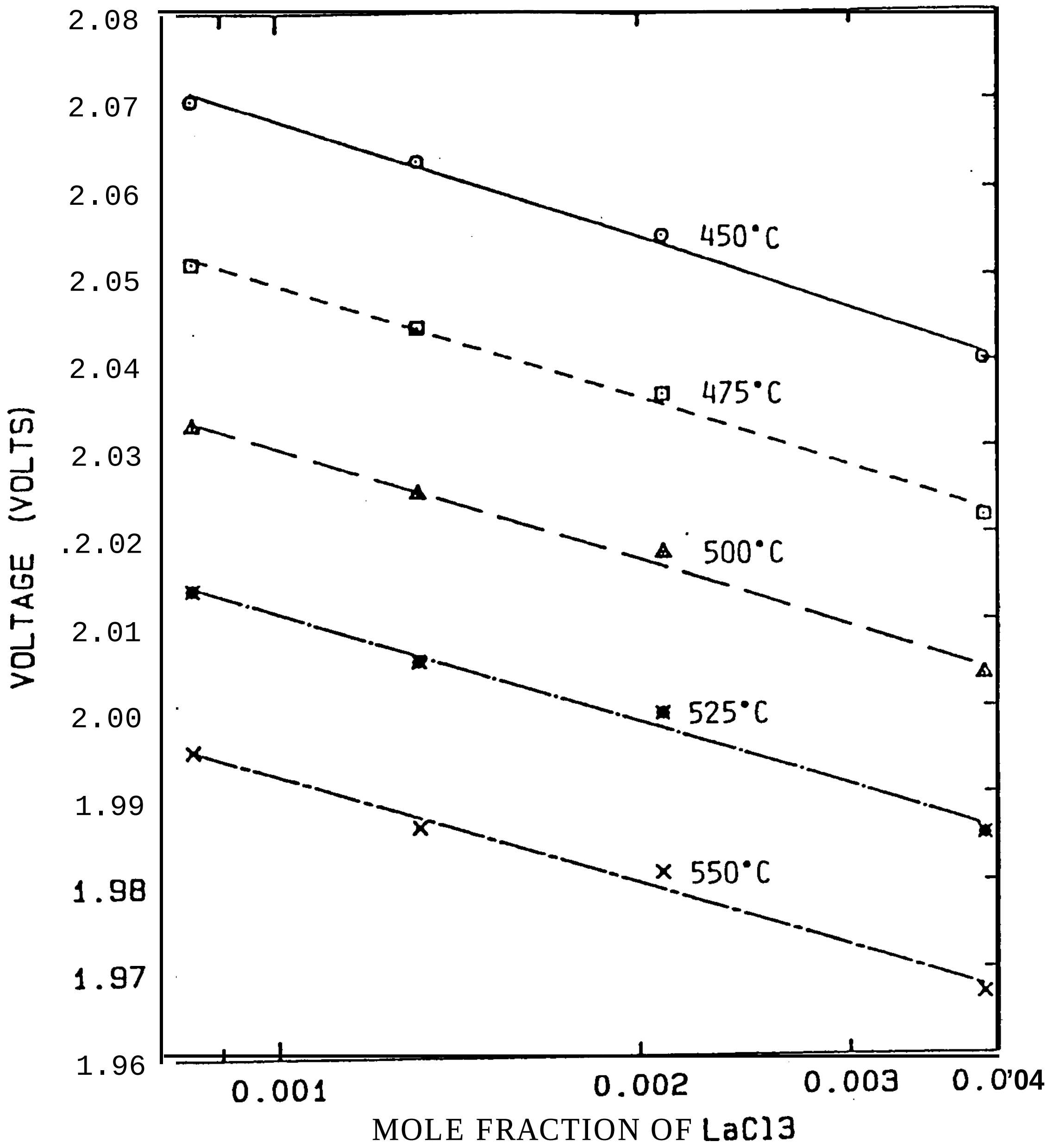
Flow Diagram of Pyrometallurgical Process for Partitioning of TRUs from HLW





A : Thermocouple
B : Cd Electrode
C : Ag/AgCl Electrode
D : Rare Earth Electrode
E : LiCl-KCl Eutectic Salt
F : Stirrer

Electrochemical Cell



Variation of Lanthanum-Silver Chloride Reference Voltages with Lanthanum Chloride Concentration

Calculation of The Activity Coefficients of Lanthanum Chloride in LiCl-KCl eutectic Salt

From the Nemst equation

$$E = E" + \frac{RT}{nF} Ln \frac{X_{La^{3+}} \cdot \gamma_{La^{3+}}}{X_{La} \cdot \gamma_{La}} \quad (1)$$

. The values Of X_{La}, γ_{La}, $X_{La^{3+}}$ and n are 1,1,1 and 3 respectively. Thus, equation (1) becomes:

$$Ln\ y_{La^{3+}} = \frac{3F(E_{X=1} - E")}{RT} \quad (2)$$

where E^{0} is the standard electrode potential

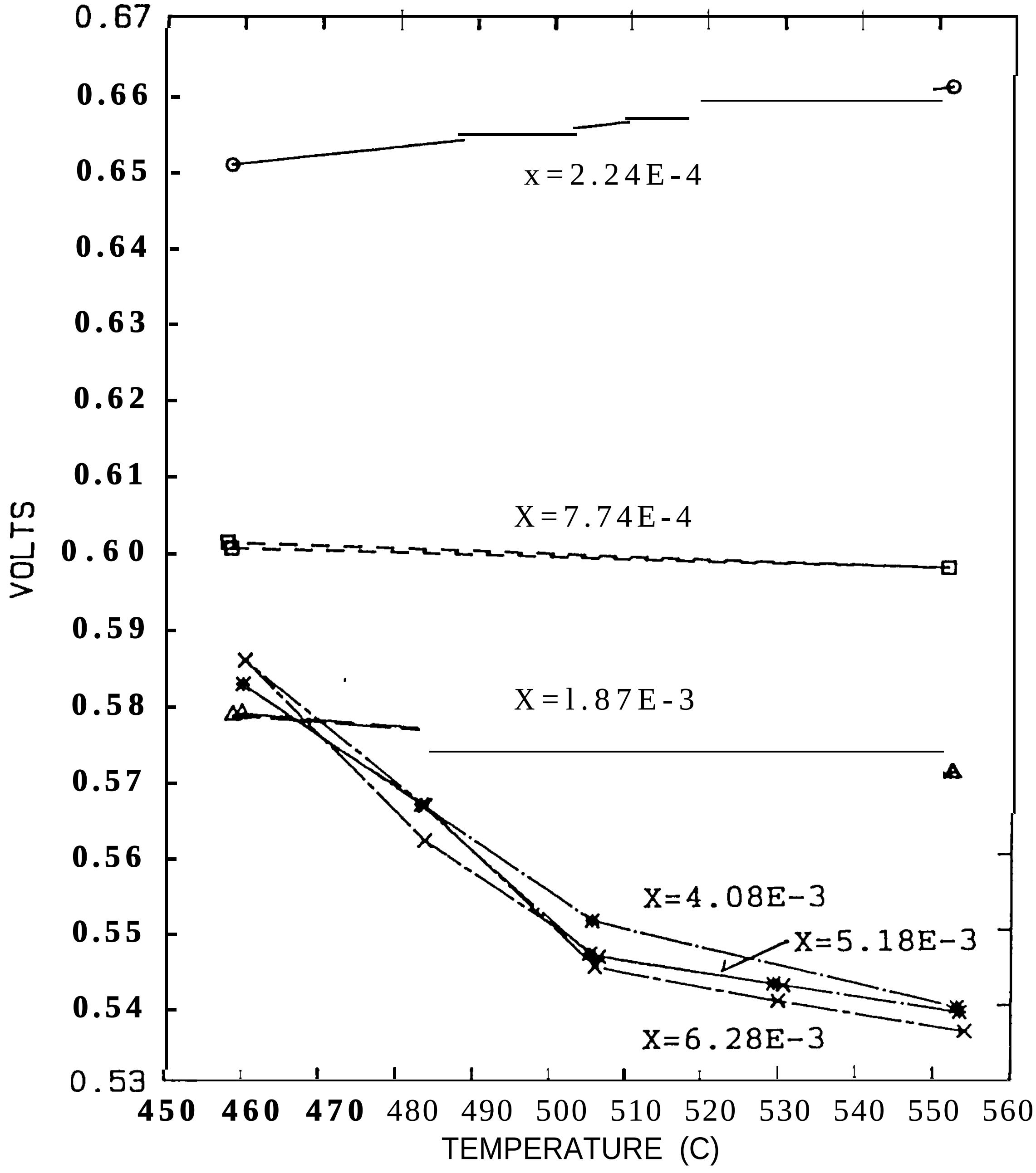
$$(E° = \Delta G_f° / nF)$$

$\Delta G_f°$ is the calculated standard free energy of formation of the supercooled liquid $LaCl_3$

Activity coefficients for rare earth chlorides in LiCl-KCl eutectic salt at 450 ℃

Element	$-\Delta G_f$ Sc.liq kcal/mol *	Activity coefficient γ
La	209.3	4.7×10^{-3}
Ce	205.1	1.5×10^{-3}
Pr	206.0	3.3×10^{-3}
Nd	203.1	1.8×10^{-2}
Gd	197.0	7.8×10^{-5}
Y	196.3	6.3×10^{-6}

* L.B.Pankratz,"Thermodynamic Properties of Halides," Bulletin 674, US Bureau of Mines (1984).



Potential Difference between La and La Dissolved in Cadmium

Calculation of The Activity Coefficients of Lanthanum Metal in Cadmium

The potential of La electrode is given by :

$$E_{La} = E^{\circ}_{La} + \frac{RT}{nF} \, Ln \, \frac{X_{La^{3+}} \cdot \gamma_{La^{3+}}}{X_{La} \cdot \gamma_{La}} \qquad (1)$$

Similarly, the potential Of La - Cd electrode is given by :

$$E_{La\ in\ Cd} = E^{\circ}_{La} + \frac{RT}{nF} \, Ln \, \frac{X_{La^{3+}} \cdot \gamma_{La^{3+}}}{X_{La\ in\ Cd} \cdot \gamma_{La\ in\ Cd}} \qquad (2)$$

From equations (1) and (2), the activity coefficient of La metal in cadmium is given by:

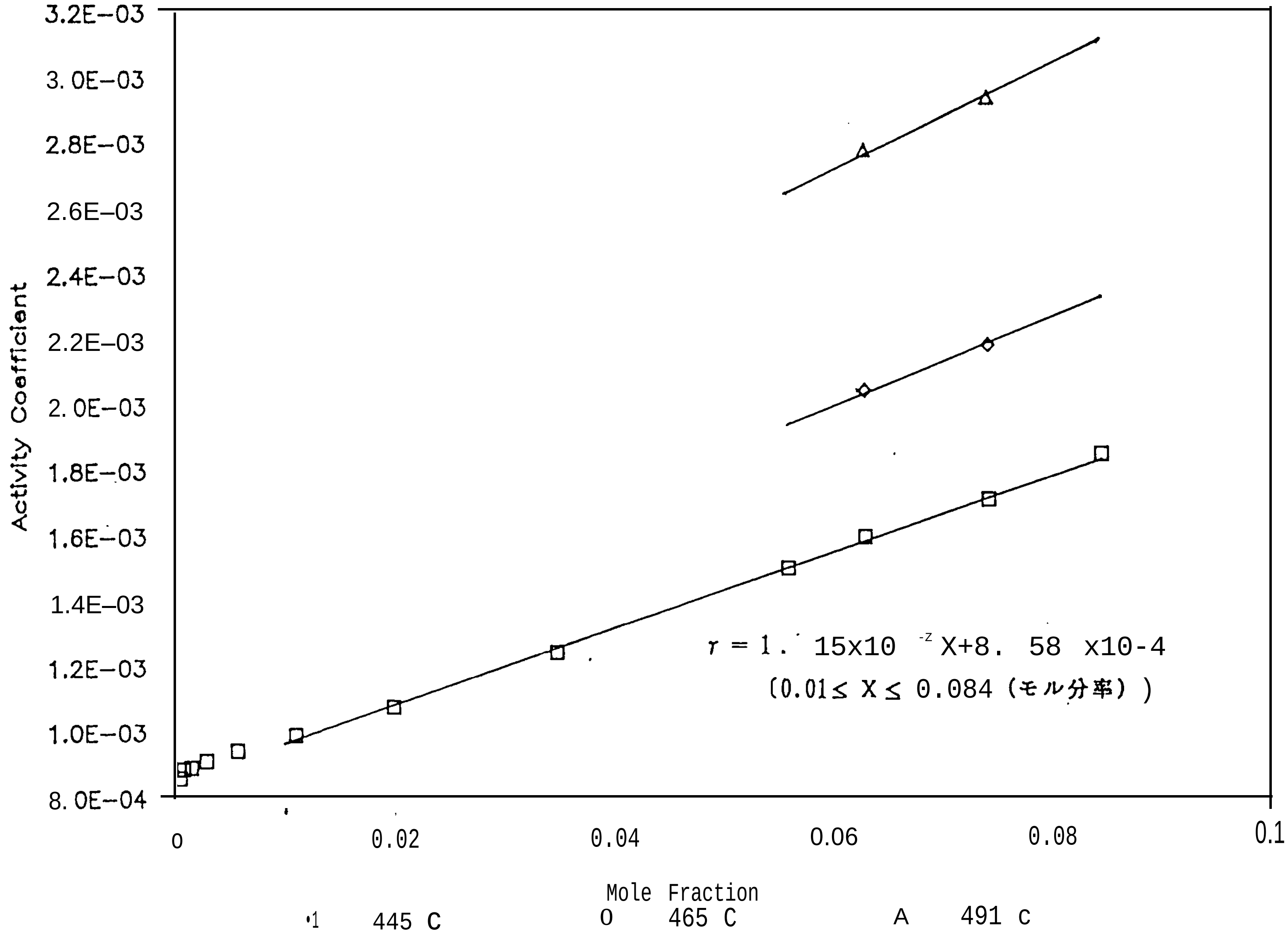
$$\gamma_{La\ in\ Cd} = \frac{\exp(3F \cdot \Delta E / RT)}{X_{La\ in\ Cd}} \qquad (3)$$

where $\Delta E = E_{La} - E_{La\ in\ Cd}$

Activity coefficients for rare earth metals in cadmium at 45o **“C**

Element	Solubility limit * at. %	Evaluated concentration at. %	Activity coefficient Y
La	9.3 X10-2	7.7 X10-2	4 XIO-1*
Ce	$1.8x10^{-1}$	$1.6x10^{-1}$	5×10^{-10}
Pr	3.0 X10-1	1.4 X10-1	2 X10-9
Nd	5.1 X10-1	$2.4x10^{-1}$	$6 x10^{-9}$
Gd	$8.5 x10^{-1}$	2.0×10^{-1}	3 X10-8
Y	NA	$2.5x10^{-1}$	3 X10-7

* R. D. Elliott,’’Constitution of Binary Alloys, First Supplement,’’McGraw-Hill Inc.(1985)



Activity coefficients for Li in Cadmium

Calculation of distribution coefficients of RE elements in the reductive extraction process

Reaction for the reductive extraction is :

$$RECl_3 + 3\,Li_{in\,Cd} = RE_{in\,Cd} + 3\,LiCl$$

Equilibrium constant of the reaction is given by :

$$K_D = Exp(-\Delta G^\circ / R\,T)$$

$$= \frac{X_{RE\,in\,Cd} \cdot (X_{Li^+})^3}{X_{RE^{3+}} \cdot (X_{Li\,in\,Cd})^3} \cdot \frac{\gamma_{RE\,in\,Cd} \cdot (\gamma_{Li^+})^3}{\gamma_{RE^{3+}} \cdot (\gamma_{Li\,in\,Cd})^3} \qquad (1)$$

The distribution coefficients are defined as :

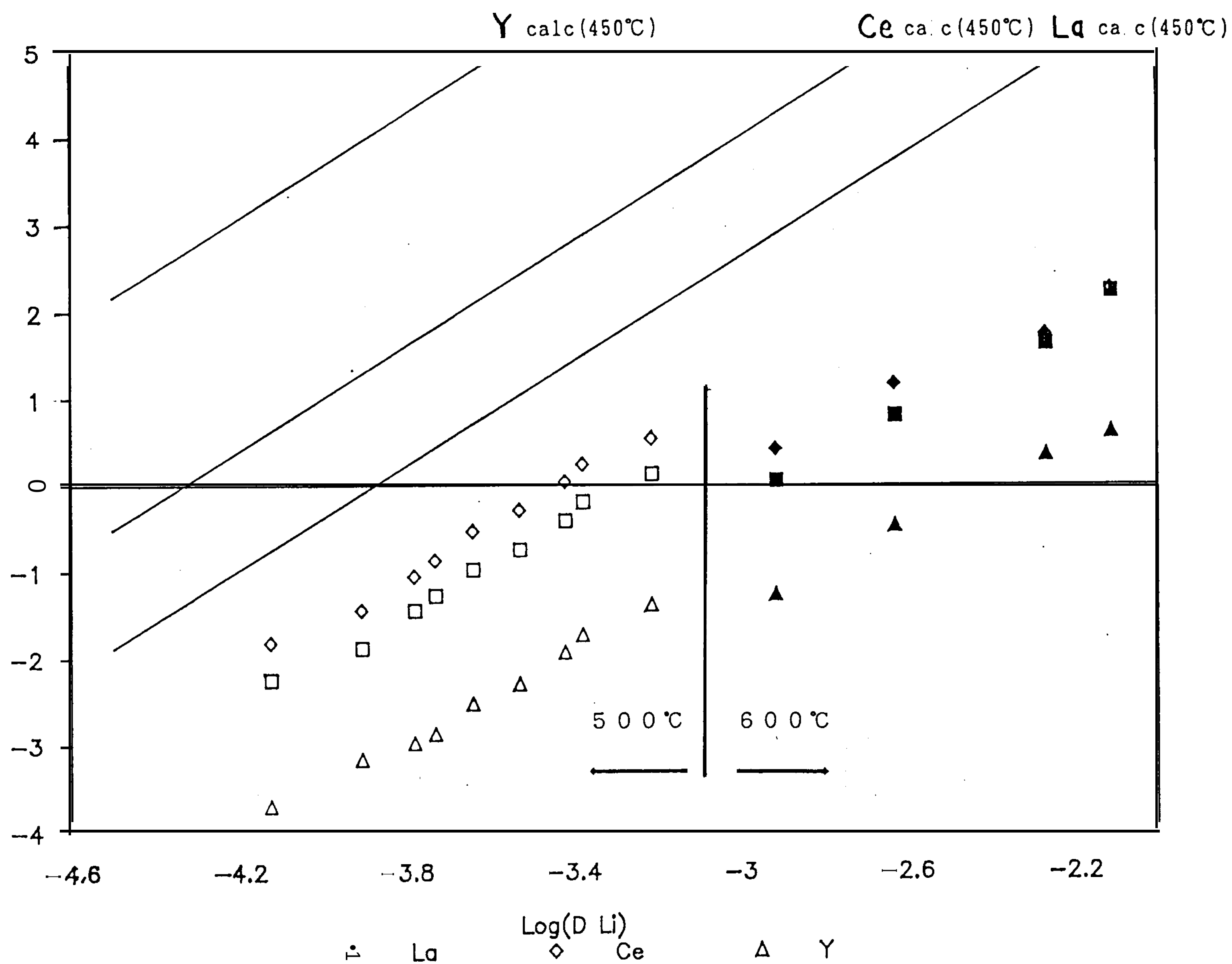
$$D_{RE} = X_{RE\,in\,Cd} / X_{RE^{3+}} \quad \text{and}$$

$$D_{Li} = X_{Li\,in\,Cd} / X_{Li^+}$$

Equation (1) can be rearranged as :

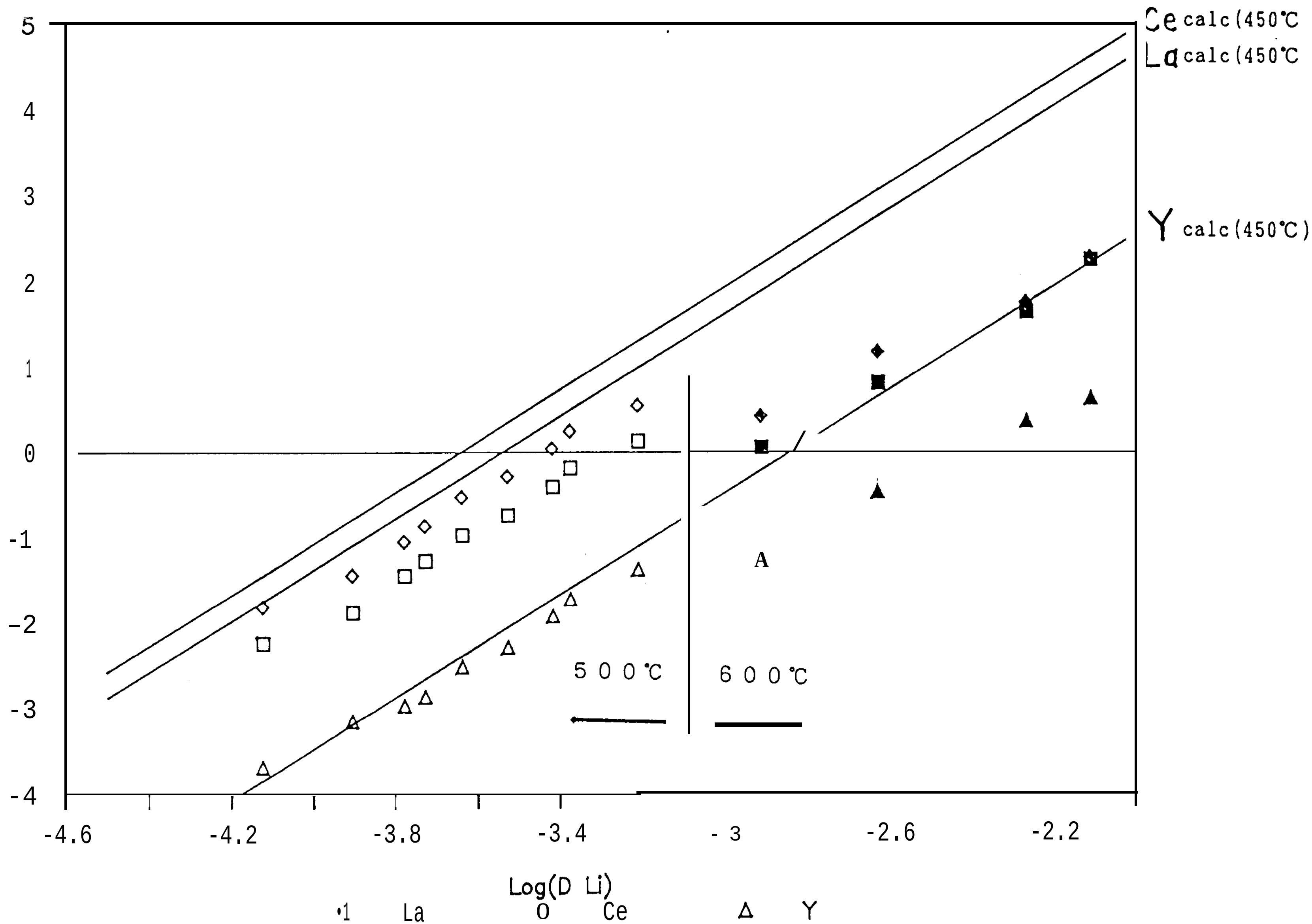
$$\log D_{RE} = 3 \cdot \log D_{Li} + \log K_D$$

$$+ \log\left[\frac{\gamma_{RE^{3+}} \cdot (\gamma_{Li\,in\,Cd})^3}{\gamma_{RE\,in\,Cd} \cdot (\gamma_{Li^+})^3}\right] \qquad (2)$$



Relationships Between Log D_M and Log D_{Li} for La, Ce and Y

(A activity coefficients are assumed to be unity is the calculation)



Relationships Between Log D_M and Log D_{Li} for La, Ce and Y

(The measured activity coefficients are employed in the calculation)