Activity Measurement of REs and Their Alloy System using Multi-Knudsen Cell Mass Spectrometry

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Measurement of thermodynamic of RE metals in the literature

Researcher	Experimental	Object
Nikaolaenko et al. (1996)	High Temperature Calorimetric	Partial Mixing Enthalpy in liquid phase($\triangle H_i$)
Subramanian et al.(1984)	EMF Measurement	Free energy of formation of intermetallic ($\triangle G_f$)
Ackermann et al. (1962)	Knudsen method	Measurement of vapor pressure
Okabe et al. (1996)	Indirect technique involving equilibration of Y-O with reference material (Ti-O)	Measurement of partial pressure of O2 in αY solid phase

➡ Chemical affinity between oxygen and rare metals is very strong.
In case of Y, solubility of solution of oxygen in solid Y is very high concentration (14.2 at%O at 1435K)

➡ These are cause for difficulty of experiment of rare metals to obtain thermodynamic data

[Y-Fe and La-Fe alloy]

1. Formation free energy of intermetallic compound in Y-Fe alloy was reported
   (Subramannian et al.(1984))
2. And, partial mixing enthalpy of Y and La in alloy was studied in liquid phase
   (Esin et al. and Berezuskii et al)

➡ **However, activities of Y and Fe, or La and Fe in binary alloy is not reported yet.**

Objective

Measurement of activity of Y and Fe in Y-Fe alloy, and activity of La and Fe in La-Fe alloy by used multi Knudsen cell mass spectrometry

Measurement of activity by Knudsen cell mass spectrometry

Vapor pressure and Ion current

$$P_i = S_i I_i T$$

$$\frac{dN}{dt} = \frac{Ps}{\sqrt{2\pi MRT}}$$

By mass spectrometry — From Knudsen cell

P_i = partial pressure in the gas phase
T = absolute temperature
b = device sensitivity constant
σ_i = i-molecule ionization cross-section
I_i = ion current of i-species.

N_i = mole quantity, t= time (sec)
P = partial pressure in the gas phase
s_i = Area of orifice
M_i = atomic weight
R = gas constant, T = absolute temperature

By using multi Knudsen cell

$$a_i = \frac{P_i}{P_i^o} = \frac{S_i I_i T_i}{S_i^o I_i^o T_i^o}$$

If reference and specimen are same material,
Device constant and temperature can be disappeared

$$a_i = \frac{P_i}{P_i^o} = \frac{I_i}{I_i^o}$$

Activity can be obtained
by calculating ratio of ion current

Knudsen cell Mass Spectrometry

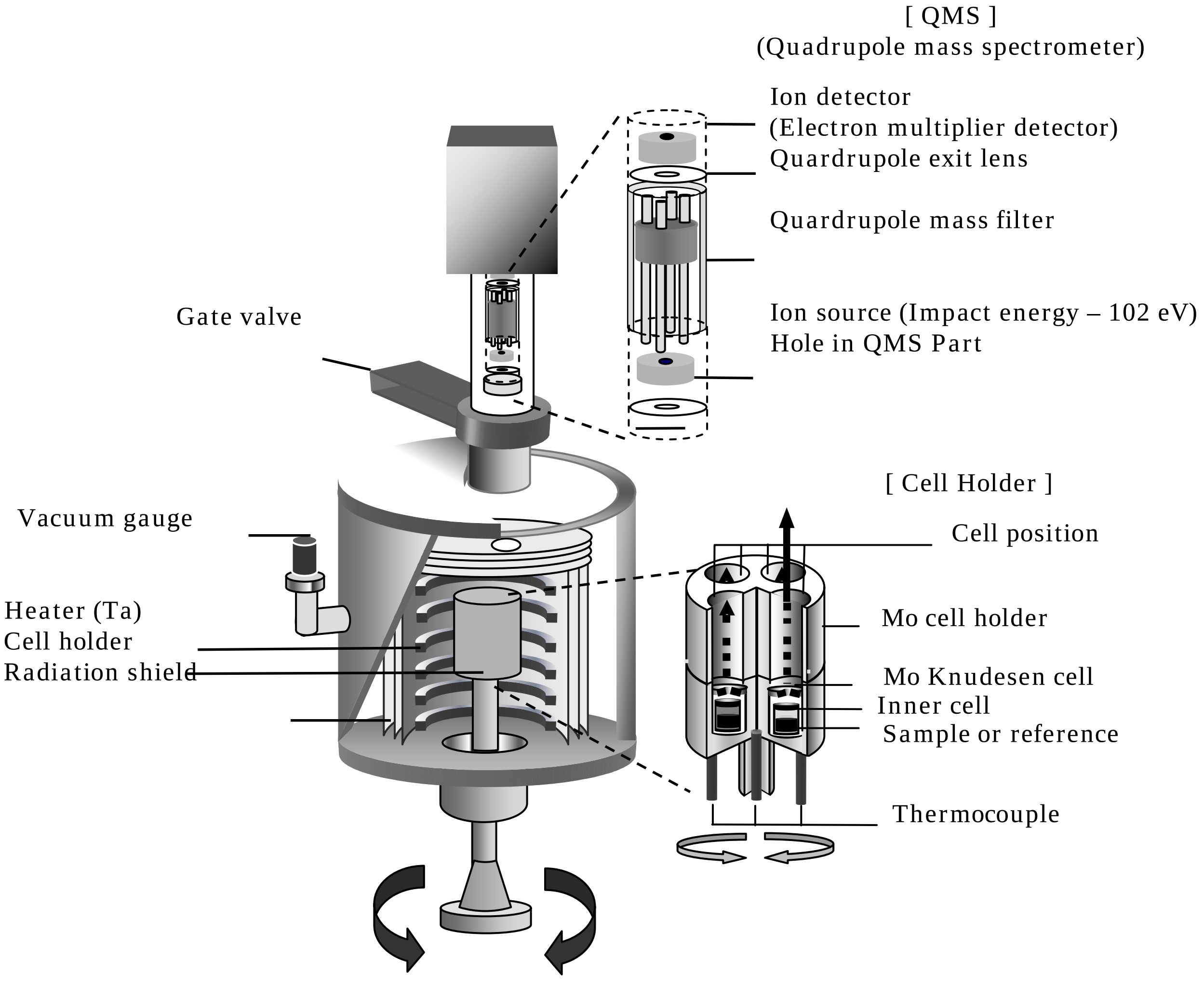
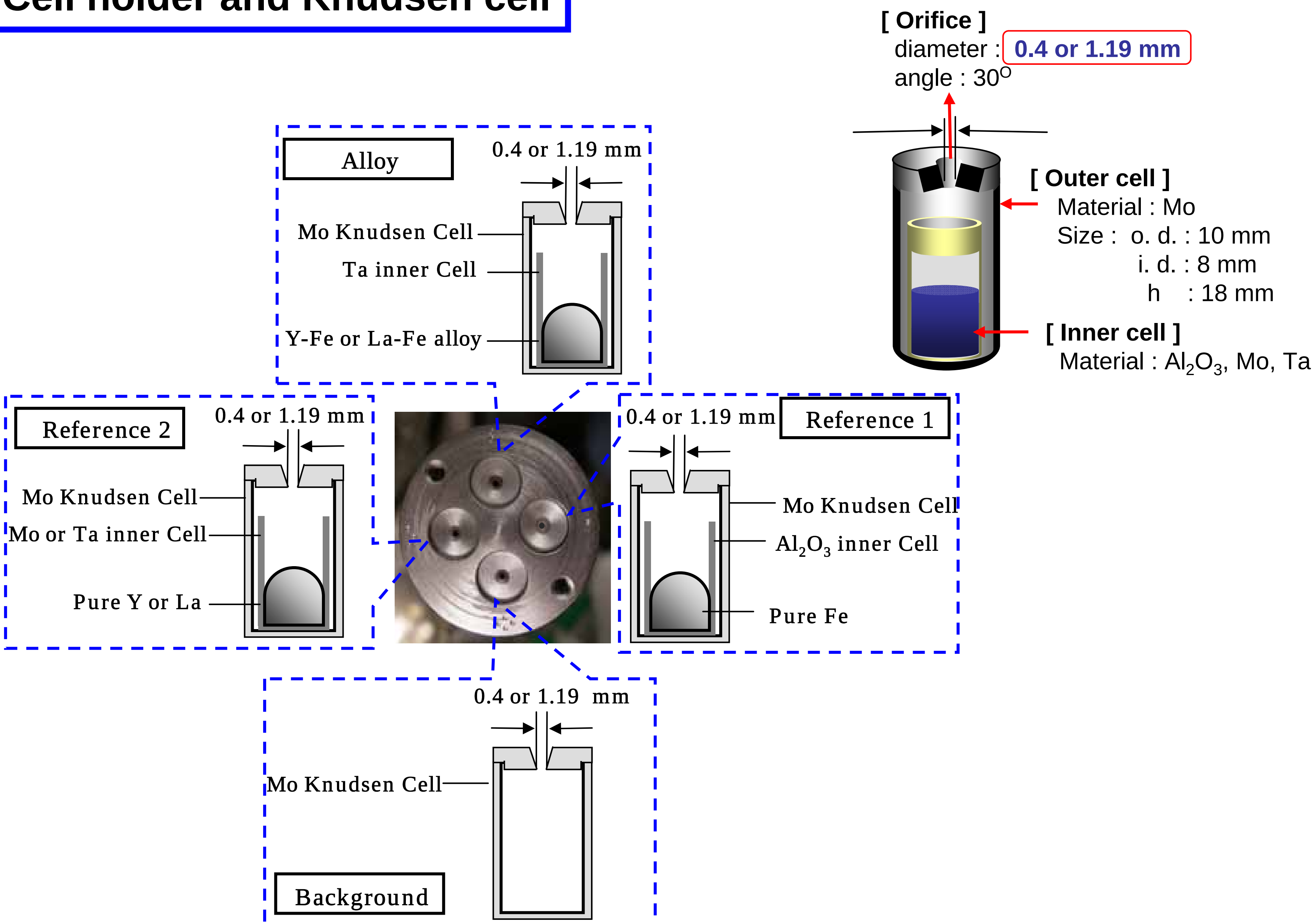
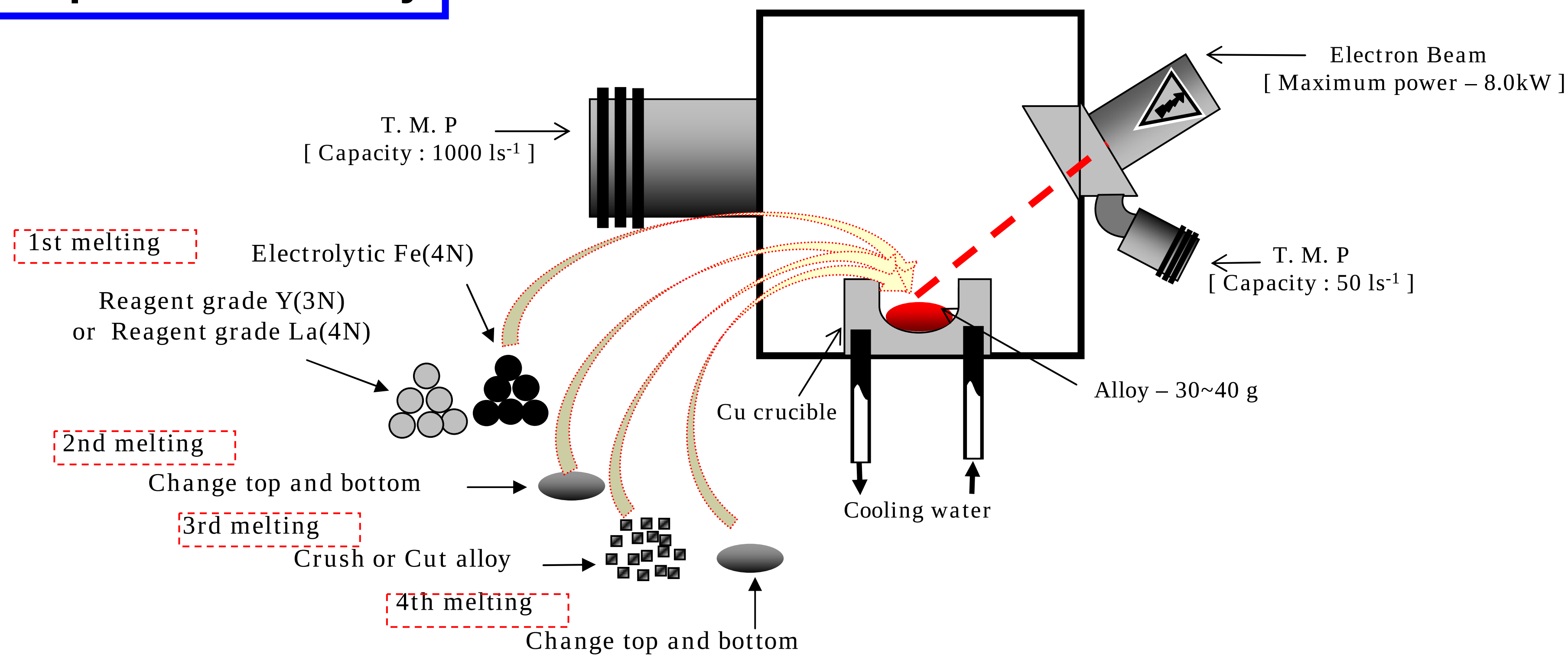


Fig. Schematic view of multi Knudsen cell mass spectrometric equipment

Cell holder and Knudsen cell



Preparation of alloy



→ ICP-AES

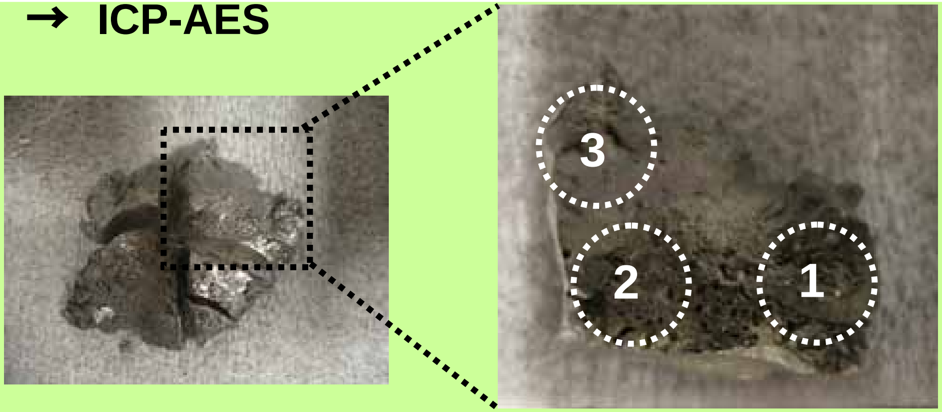


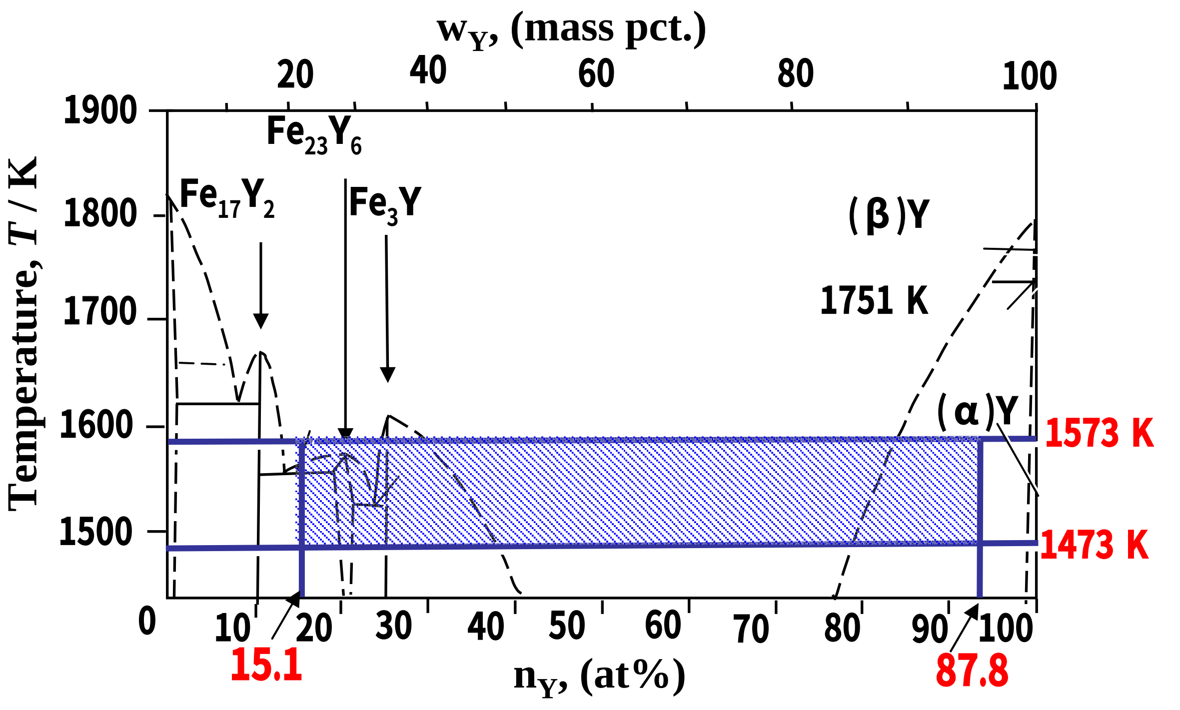
Fig. Prepared Fe-Y master alloy

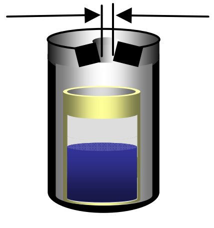
→ Confirmation of uniformity and Concentration of alloy

Specimen	Concentration of La in La-Fe alloy (at%(wt%))
1	39.3 ± 0.1 (61.7 ± 0.3)
2	48.9 ± 0.2 (60.4 ± 0.5)
3	56.7 ± 0.1 (67.6 ± 0.3)
4	64.3 ± 0.1 (74.1 ± 0.3)
5	71.0 ± 0.2 (79.6 ± 0.5)
6	86.6 ± 0.1 (91.1 ± 0.2)
7	94.3 ± 0.4 (96.3 ± 1)

Specimen	Concentration of Y in Y-Fe alloy (at%(wt%))
1	15.1 ± 0.5 (22.1 ± 0.8)
2	23.2 ± 0.09 (32.5 ± 0.1)
3	25.3 ± 0.3 (35.0 ± 0.5)
4	49.1 ± 0.3 (60.6 ± 0.5)
5	60.7 ± 0.2 (71.1 ± 0.3)
6	70.2 ± 0.4 (78.9 ± 0.6)
7	83.3 ± 0.6 (88.8 ± 1)
8	87.8 ± 0.2 (92.0 ± 0.3)

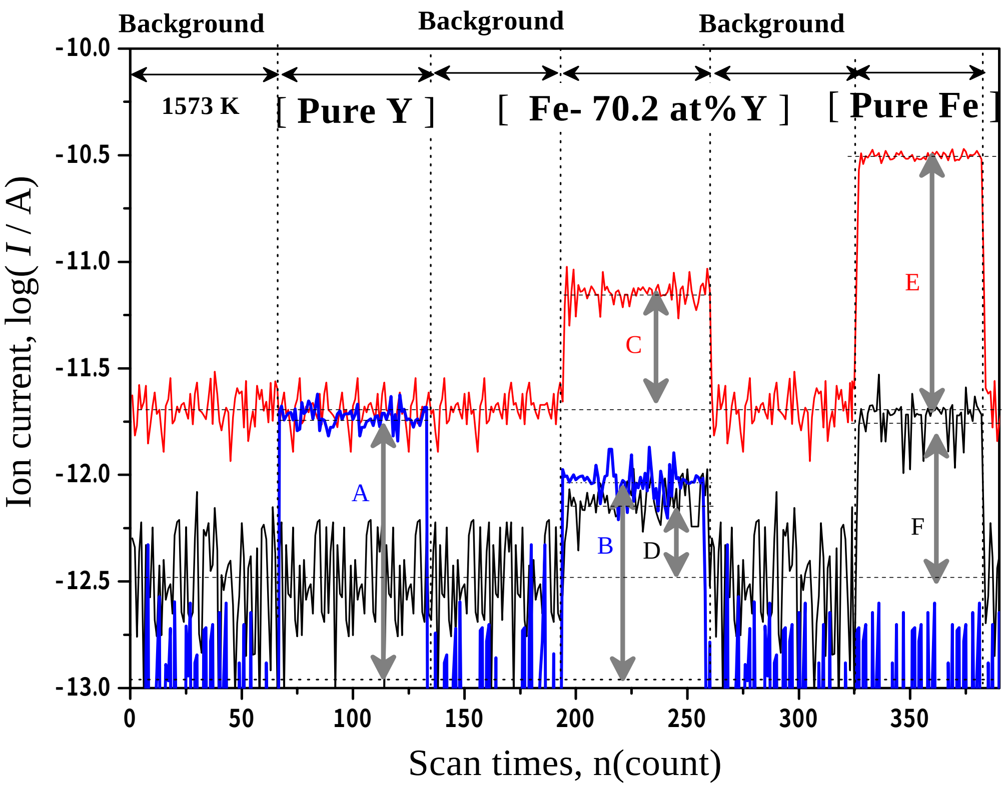
Measurement of Y-Fe alloy





- Inner cell : Mo (Y), Al_2O_3 (Fe), Ta (Y-Fe alloy)
- Diameter of orifice : 0.4 mm
- Reference : Y (99.99%)、electronic Fe (99.99%)

Measurement of ion currents of Y and Fe



For pure Y

A : I_{89} for Y (= (1.79 ± 0.20) × 10^{-12})

For Y-Fe alloy

B : I_{89} for Y (= (8.60 ± 1.46) × 10^{-13})

C : I_{56} for Fe (= (5.72 ± 1.04) × 10^{-12})

D : I_{54} for Fe (= (3.61 ± 1.54) × 10^{-13})

For pure Fe

E : I_{56} for Fe (= (2.46 ± 0.13) × 10^{-11})

F : I_{54} for Fe (= (1.54 ± 0.34) × 10^{-12})

$$a_Y = \frac{I_{\text{Y in Y-Fe alloy}}}{I^o_{\text{Pure Y}}}$$

$$a_{Fe} = \frac{I_{\text{Fe in Y-Fe alloy}}}{I^o_{\text{Pure Fe}}}$$

Isotope of Y : ^{89}Y = 100%

$$I_Y = I_{89}$$

Isotope of Fe : ^{56}Fe (91.72%), ^{54}Fe (5.8%), ^{57}Fe (2.2%), ^{58}Fe(0.28%)

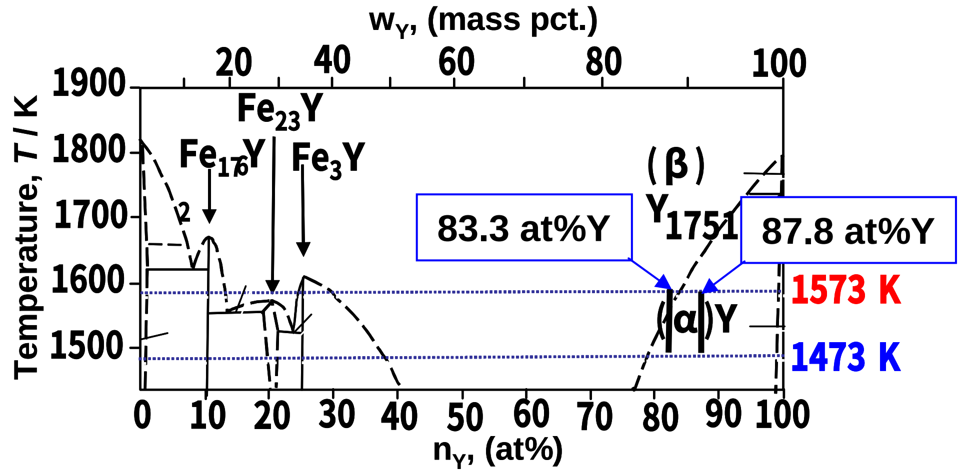
$$I_{Fe} = (I_{56} + I_{54})$$

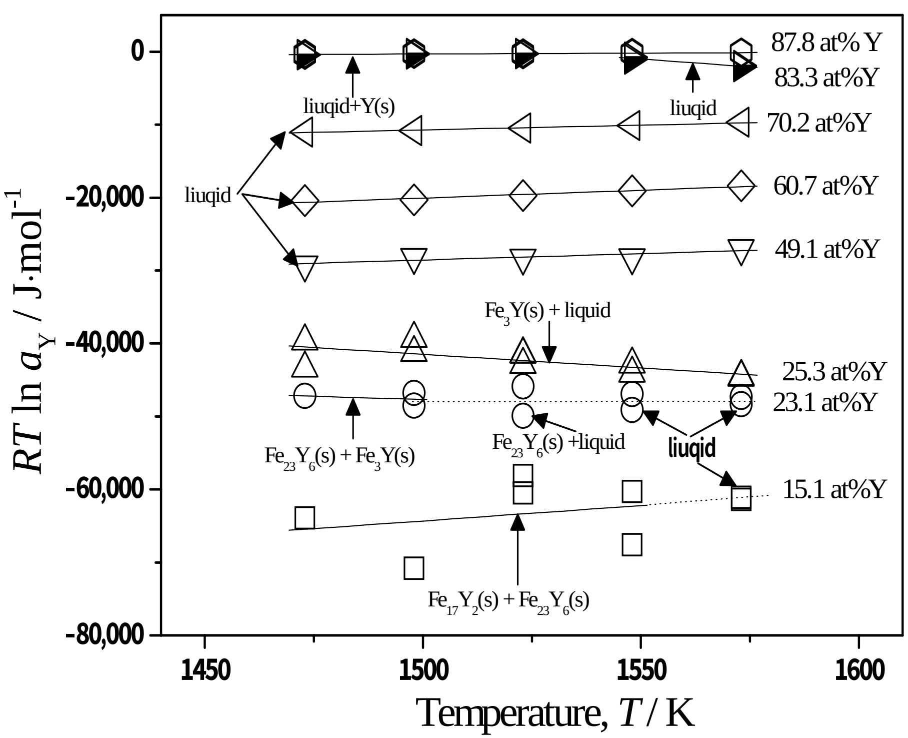
I_{56}/I_{54} = 15.97 for Fe in pure Fe

I_{56}/I_{54} = 15.87 for Fe in Y-Fe alloy

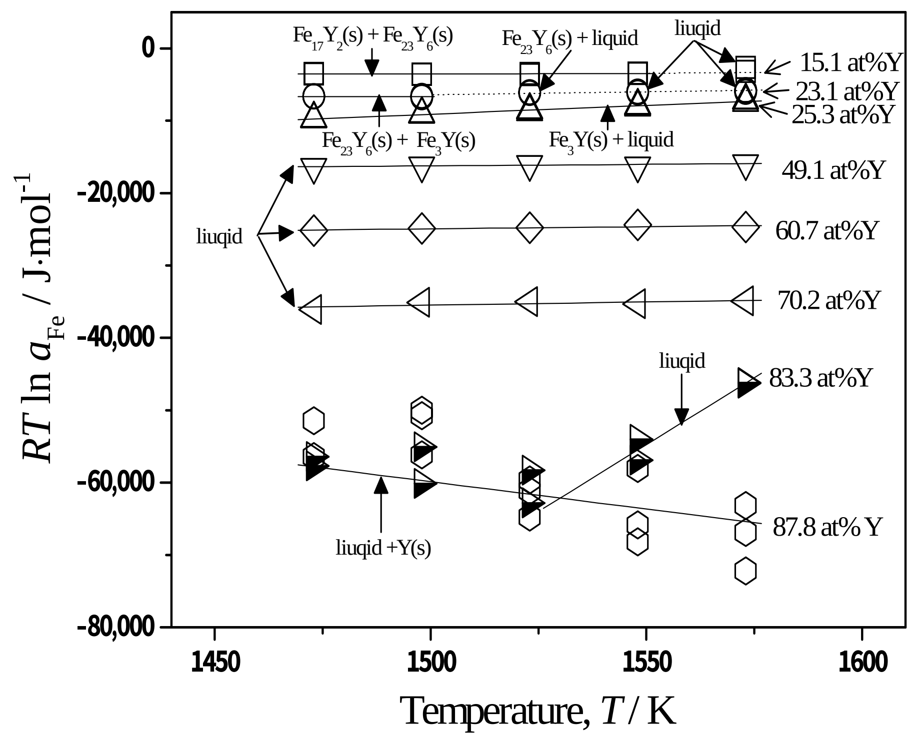
Natural abundance :

^{54}Fe / ^{56}Fe =15.81.

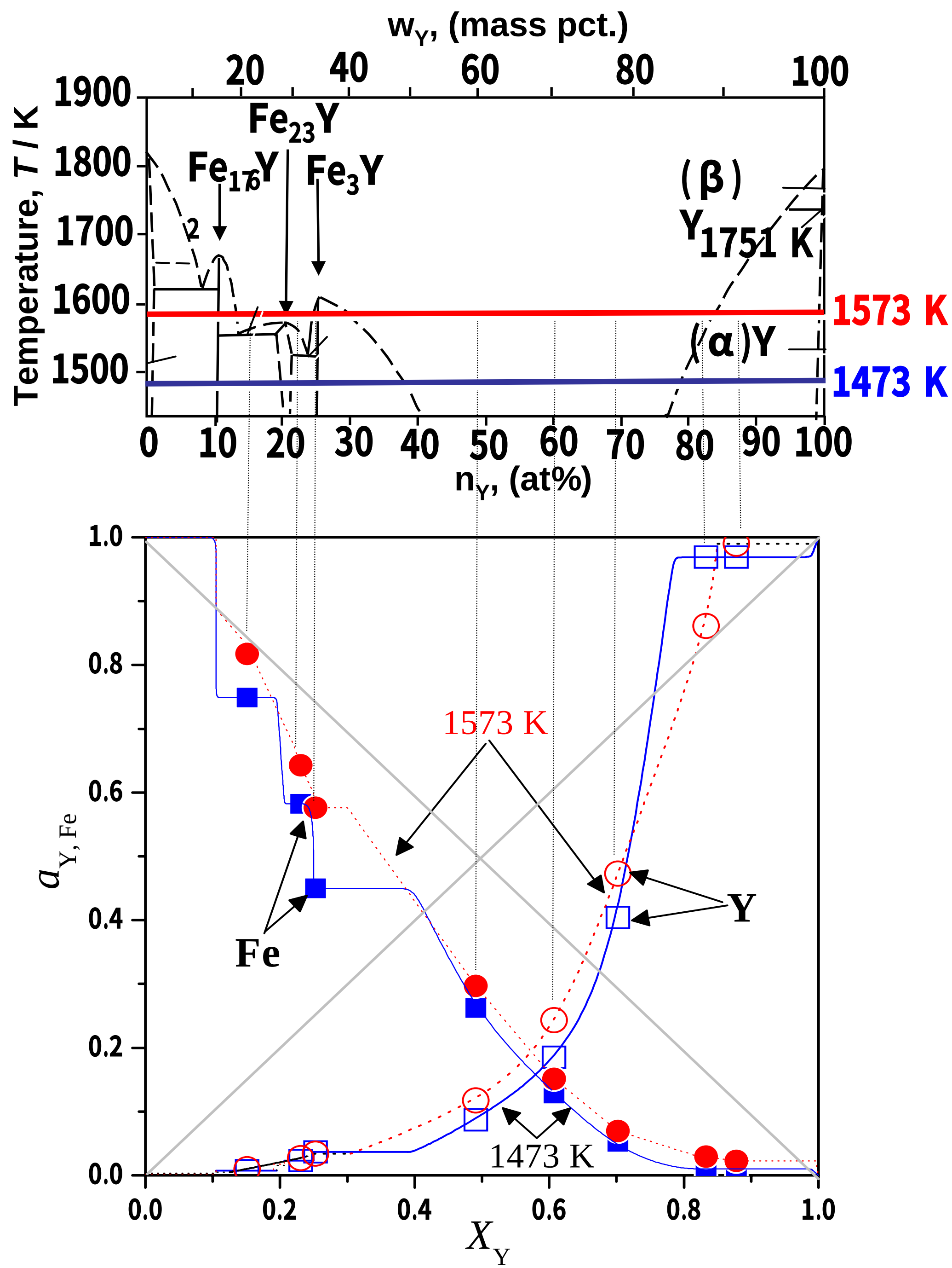




a) Activity of Y

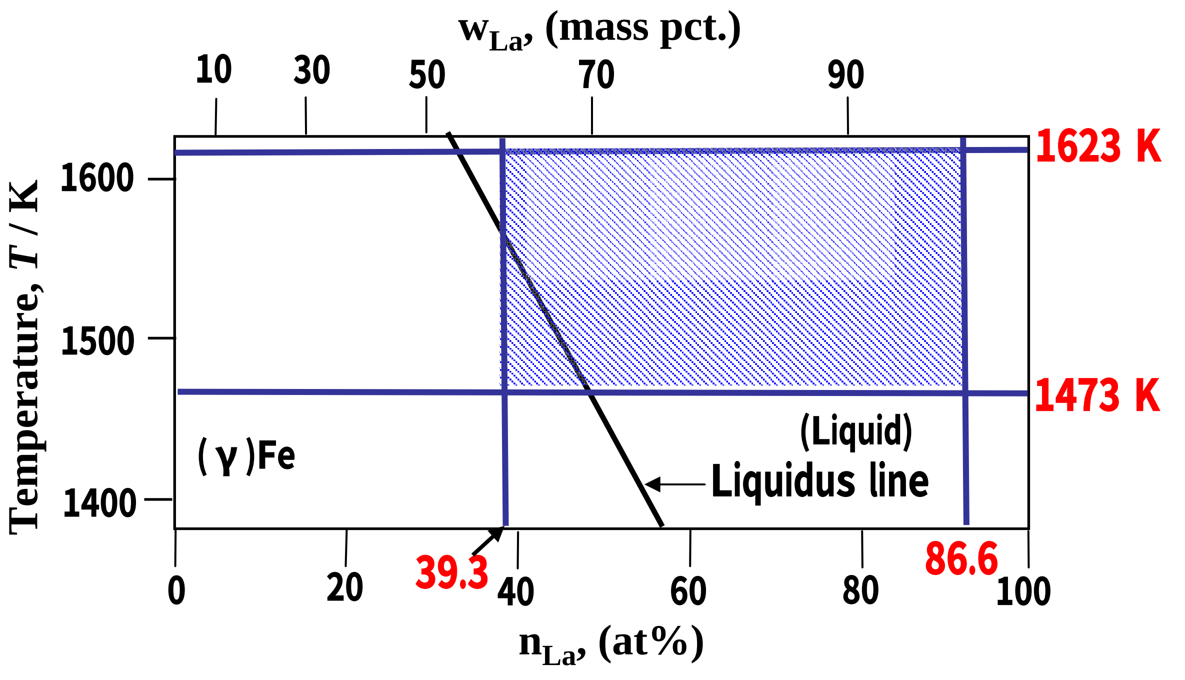


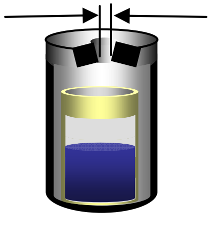
b) Activity of Fe



w_Y, (mass pct.)
20
40
60
80
100
1900
1800
1700
1600
1500
Temperature, T / K
Fe23Y
Fe17Y
Fe3Y
(β)
Y
1751 K
1573 K
(α)Y
1473 K
0
10
20
30
40
50
60
70
80
90
100
n_Y, (at%)
1.0
0.8
0.6
0.4
0.2
0.0
a_Y, Fe
1573 K
Y
Fe
1473 K
0.0
0.2
0.4
0.6
0.8
1.0
X_Y

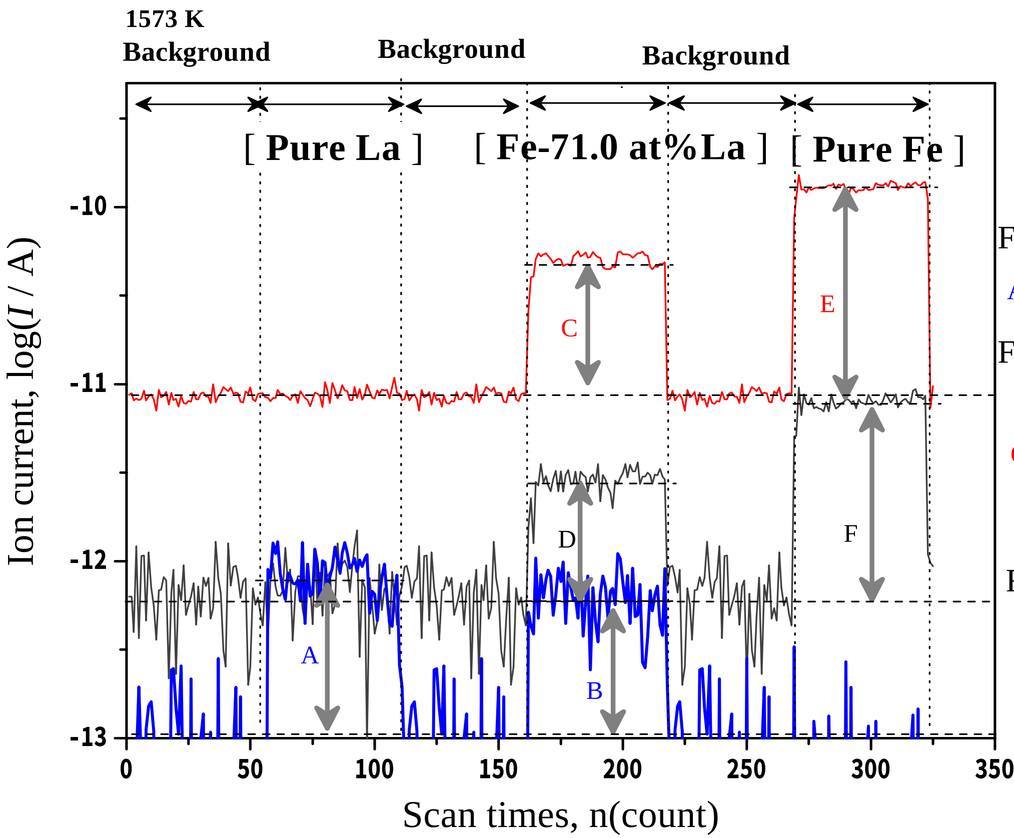
Measurement of La-Fe alloy





- Inner cell : Ta (La and La-Fe alloy), Al_2O_3 (Fe)
- Diameter of orifice : 1.19 mm
- Reference : La (99.99%)、electronic Fe(99.99%)

Measurement of ion currents of La and Fe



For pure La

A : I_{139} for La (= (8.17 ± 2.59) × 10^{-13})

For La-Fe alloy

B : I_{139} for La (= (6.72 ± 2.18) × 10^{-13})

C : I_{56} for Fe (= (3.47 ± 0.76) × 10^{-11})

D : I_{54} for Fe (= (2.18 ± 0.52) × 10^{-12})

For pure Fe

E : I_{56} for Fe (= (1.14 ± 0.064) × 10^{-10})

F : I_{54} for Fe (= (7.21 ± 0.70) × 10^{-12})

$$a_{La} = \frac{I_{\text{La in La-Fe alloy}}}{I^{o}_{\text{Pure La}}}$$

$$a_{Fe} = \frac{I_{\text{Fe in La-Fe alloy}}}{I^{o}_{\text{Pure Fe}}}$$

Figure Measurement of ion currents of La, Fe from pure La, Fe and La-Fe alloy by rotating cell holder

Laの同位体 ： ^{139}La (99.91%), ^{138}La (0.09%),

$\Rightarrow$ $I_{La} = (I_{139})$

Isotope of Fe： ^{56}Fe (91.72%), ^{54}Fe (5.8%), ^{57}Fe (2.2%), ^{58}Fe(0.28%)

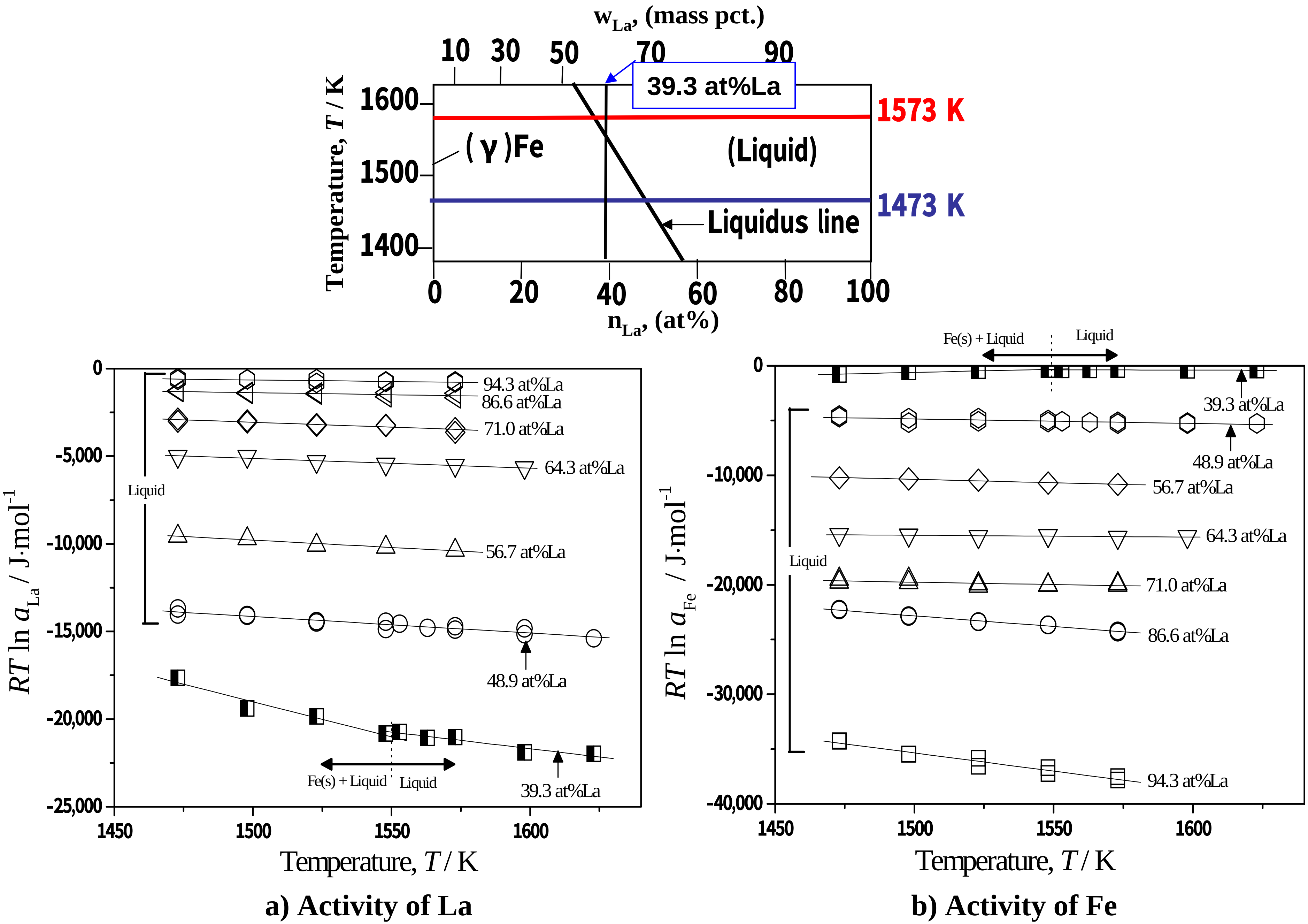
$\Rightarrow$ $I_{Fe} = (I_{56} + I_{54})$

I_{56}/I_{54} = 15.81 for Fe in pure Fe

I_{56}/I_{54} = 15.92 for Fe in La-Fe alloy

Natural abundance ：

^{54}Fe / ^{56}Fe =15.81.


w_La, (mass pct.)
10
30
50
70
90
39.3 at%La
1600
1500
1400
Temperature, T / K
1573 K
1473 K
(γ)Fe
(Liquid)
Liquidus line
0
20
40
60
80
100
n_La, (at%)
RT ln a_La / J·mol-1
0
-5,000
-10,000
-15,000
-20,000
-25,000
1450
1500
1550
1600
Temperature, T / K
94.3 at%La
86.6 at%La
71.0 at%La
64.3 at%La
56.7 at%La
48.9 at%La
39.3 at%La
Liquid
Fe(s) + Liquid
Liquid
a) Activity of La
RT ln a_Fe / J·mol-1
0
-10,000
-20,000
-30,000
-40,000
1450
1500
1550
1600
Temperature, T / K
Fe(s) + Liquid
Liquid
39.3 at%La
48.9 at%La
56.7 at%La
64.3 at%La
71.0 at%La
86.6 at%La
94.3 at%La
Liquid
b) Activity of Fe

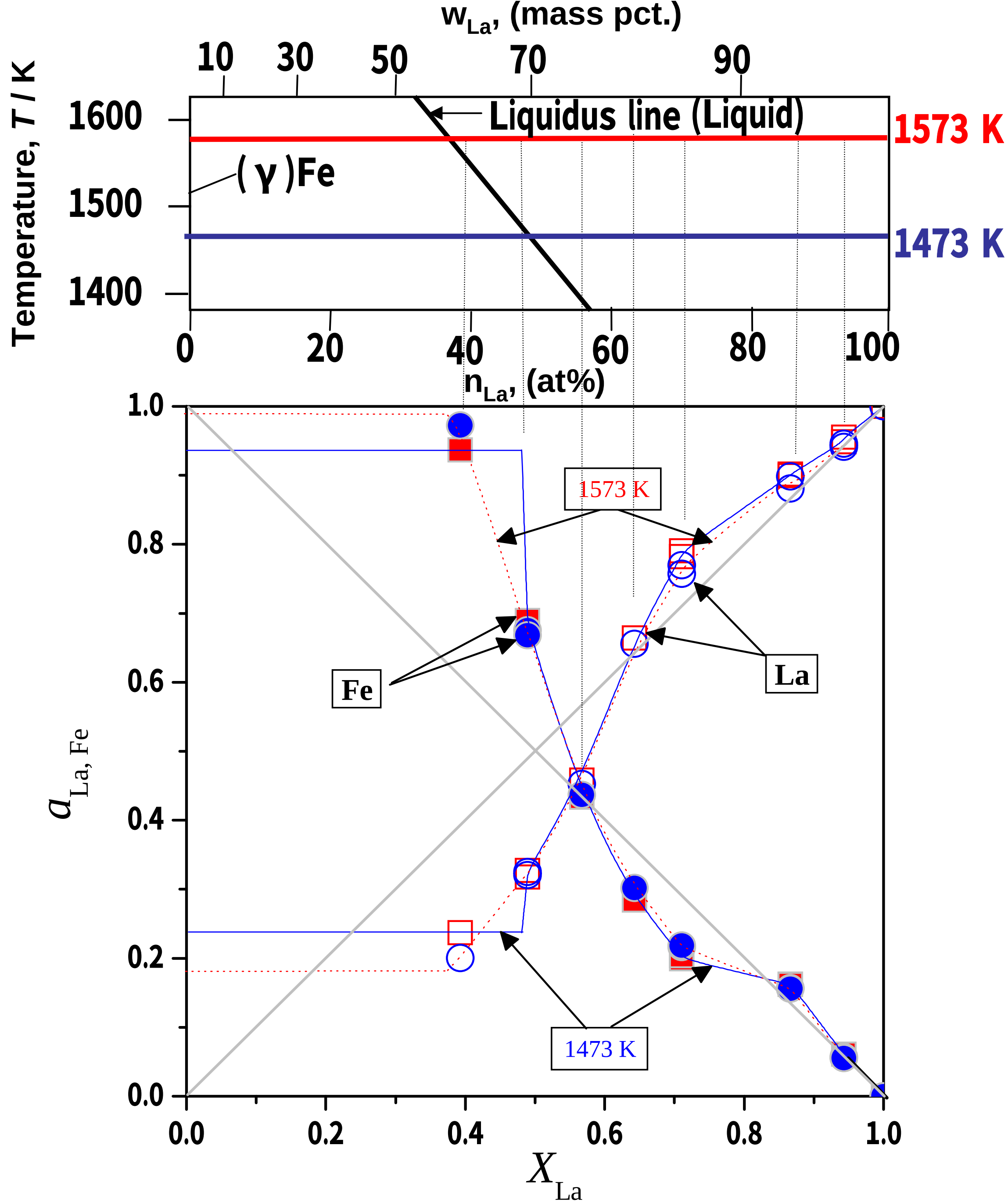
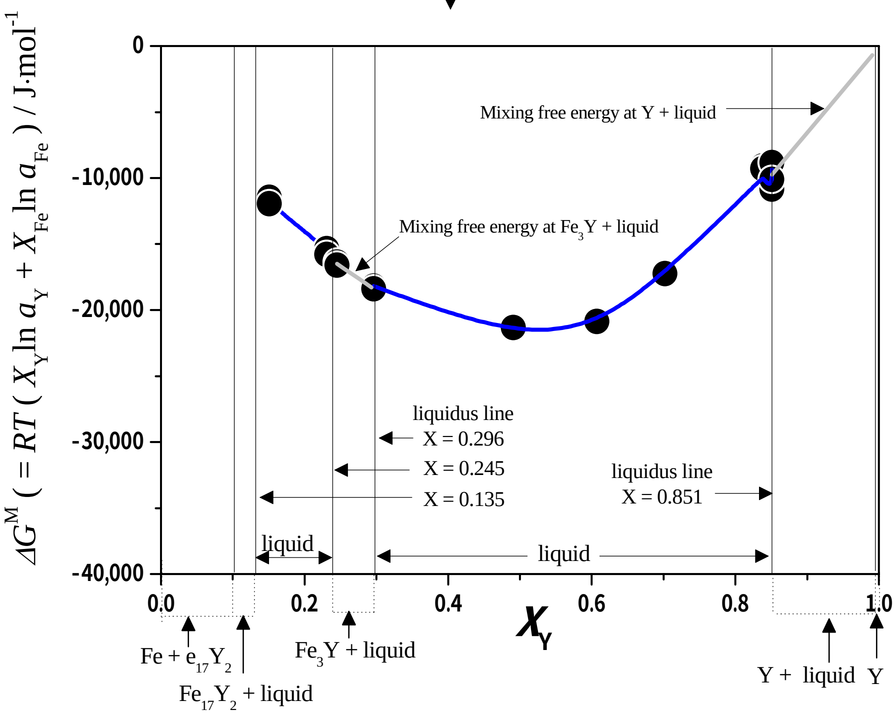


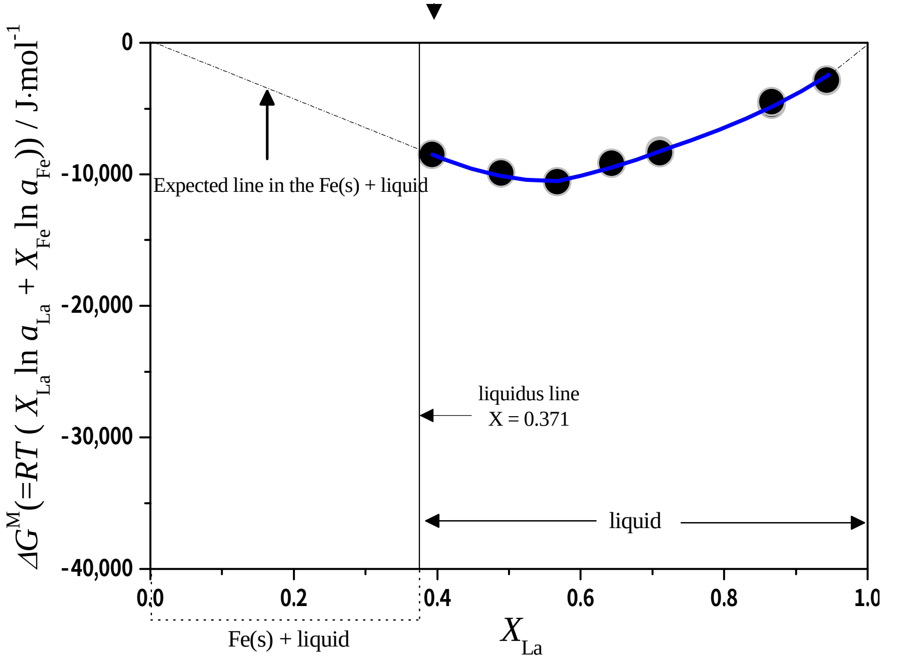
Figure. Composition dependence of activities of La and Fe in Fe-La alloy

Mixing free energy in liquid (1573 K)

$$\Delta G^{M}_{\alpha_A} = RT\,(X_A \ln a_A + X_B \ln a_B)$$



Y- Fe alloy (1573 K)



La- Fe alloy (1573 K)

Summary

1. The activities of Y and Fe in Y-Fe alloy were measured in the range of temperature from 1473 to 1573 K

2. The activities of La and Fe in La-Fe alloy were measured in the range of temperature from 1473 to 1623 K

3. Mixing free energy of Y-Fe and La-Fe alloy was calculated in the liquid phase