QA III

Diagrama Generalizado de Predominio de Estado Redox

DGPER

Fe^{n+} $pe = f(pH)_{pCo,\ pL}$

trazo rápido

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3.8.6 Reactividad redox-acidez-complejos-solubilidad, DGPER. Ejemplo (4). Fe^{n+} en medio complejante de fluoruro.

El Fe(III) es un catión metálico muy abundante en la naturaleza e interfiere en la obtención de otros metales de valor comercial en cantidades mucho menores. Por ello sus propiedades redox son enmascaradas solubilizando las muestras minerales con un medio de reacción de floruro de amonio concentrado para amortiguar el nivel de complejación. A concentraciones de lixiviado se cumple que $\alpha_{M^{n-i}(OH)_i} = 1$:

$$\begin{array}{ccccc} & Fe(OH)_2\downarrow & & Fe(OH)_3\downarrow & \\ & \Updownarrow & & \Updownarrow & \\ \boldsymbol{Fe^0} & \rightleftharpoons \boldsymbol{Fe^{2+} + 1e^-} & \rightleftharpoons & \boldsymbol{Fe^{3+} + 1e^-} & \\ & \Updownarrow & & \Updownarrow & \\ & FeF^+ & & Fe(F)_i^{3-i} & \end{array}$$

$$HF \rightleftharpoons F^- + H^+$$

Se conoce la siguiente información (valores redondeados):

$\log K^{2e,Fe^{2+}}_{Fe^0} = -15;$

$\log K^{1e,Fe^{3+}}_{Fe^{2+}} = 13;$

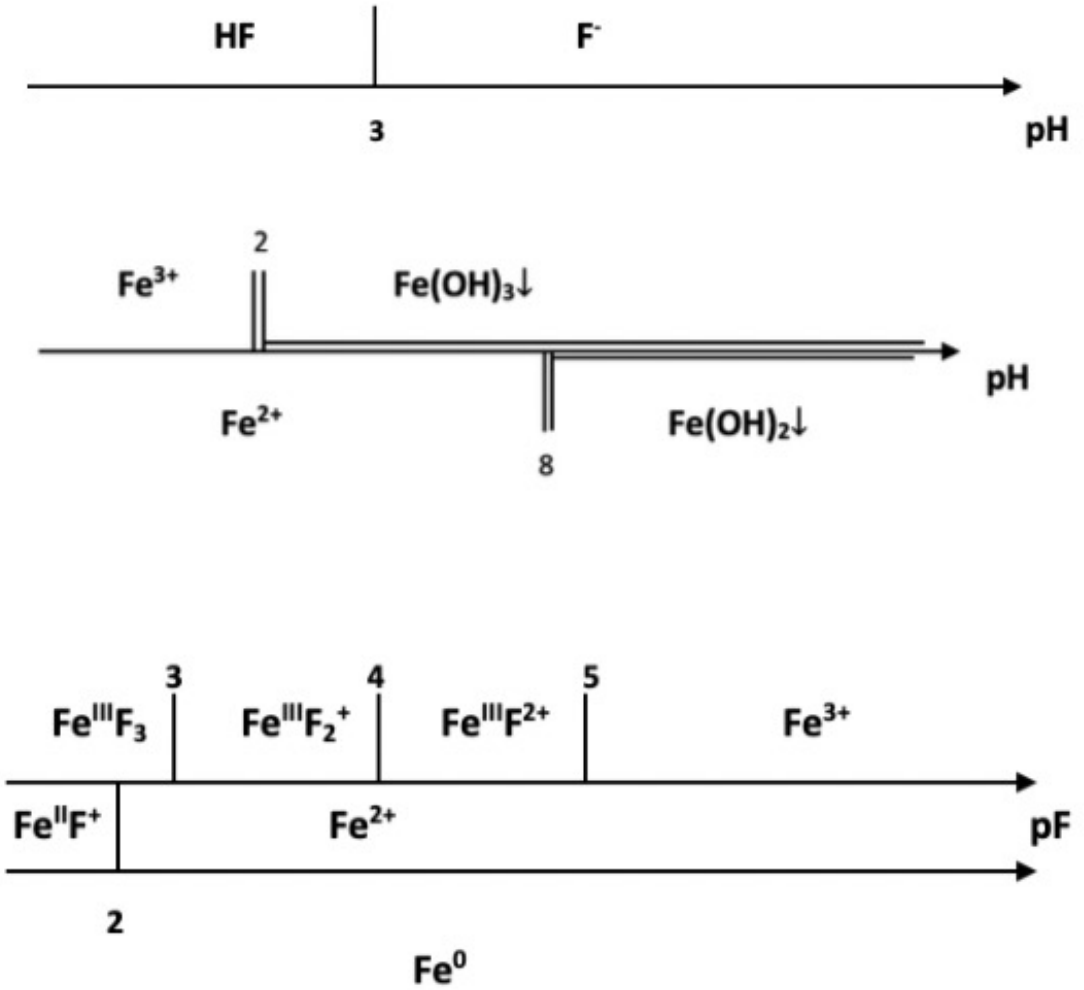
$\log K^{3OH}_{Fe(OH)_3\downarrow} = 38$

$\log K^{2OH}_{Fe(OH)_2\downarrow} = 15$

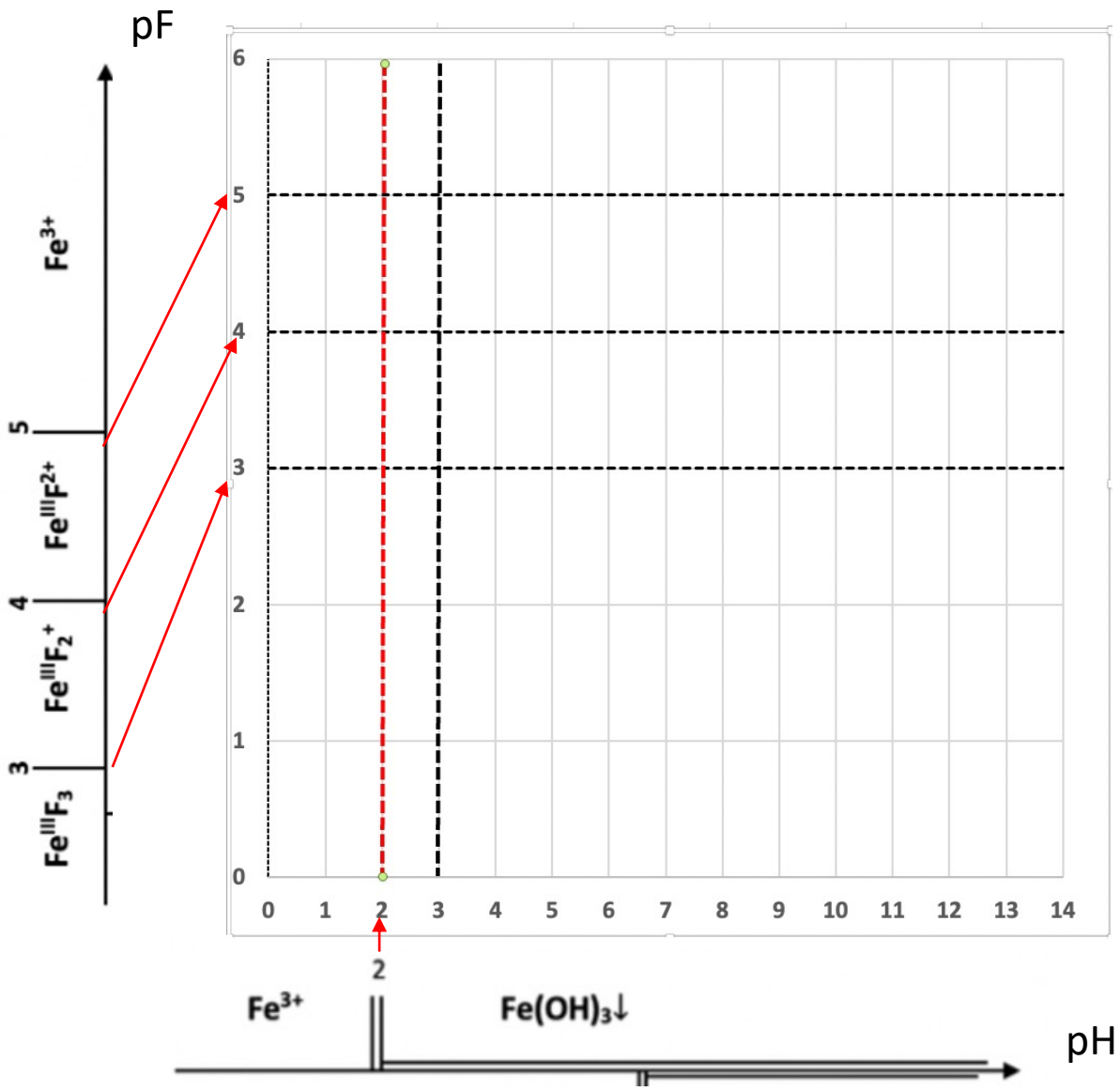
$i =$	1	2	3
$\log K^{iF}_{Fe(F)_i^{3-i}} =$	5	9	12
$\log K^{iF}_{Fe(F)_i^{2-i}} =$	2		

$\log K^{H}_{HF} = 3;$

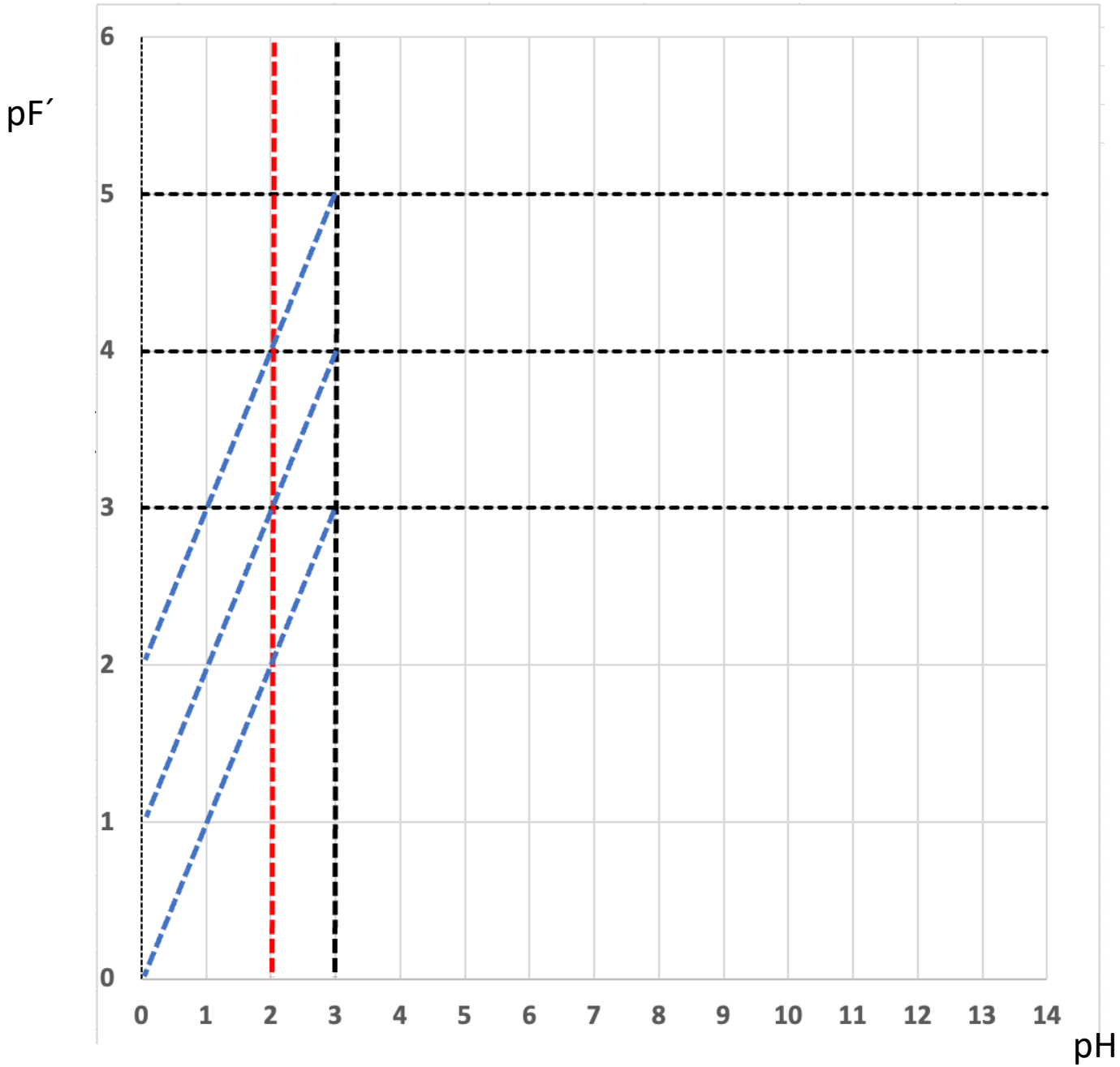
Para pCo = 2, los valores de pH y pL = pF de transición de especies y de estado están representados por sendos DUZPE combinados:



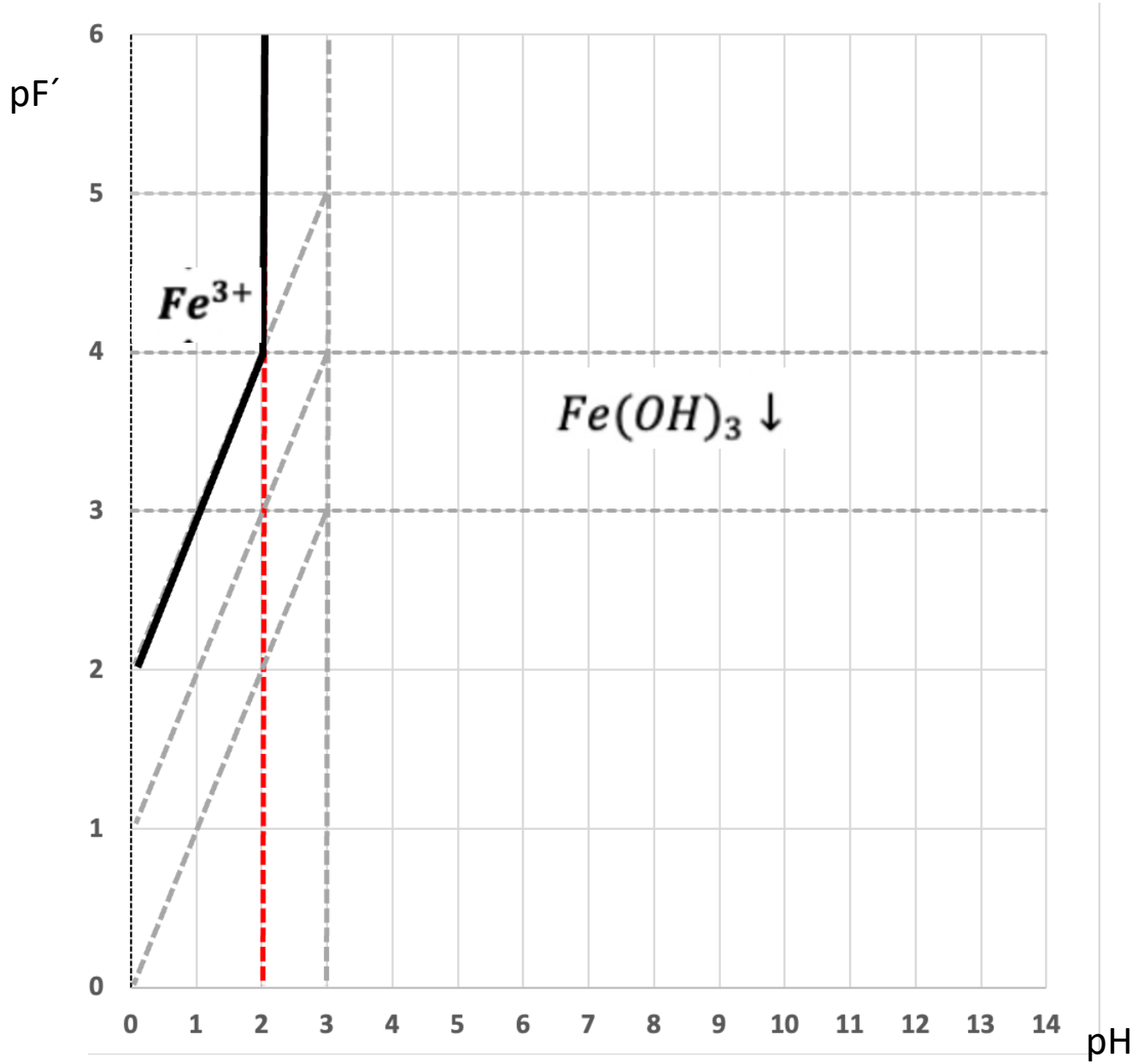
1) lineas guía Fe(III):



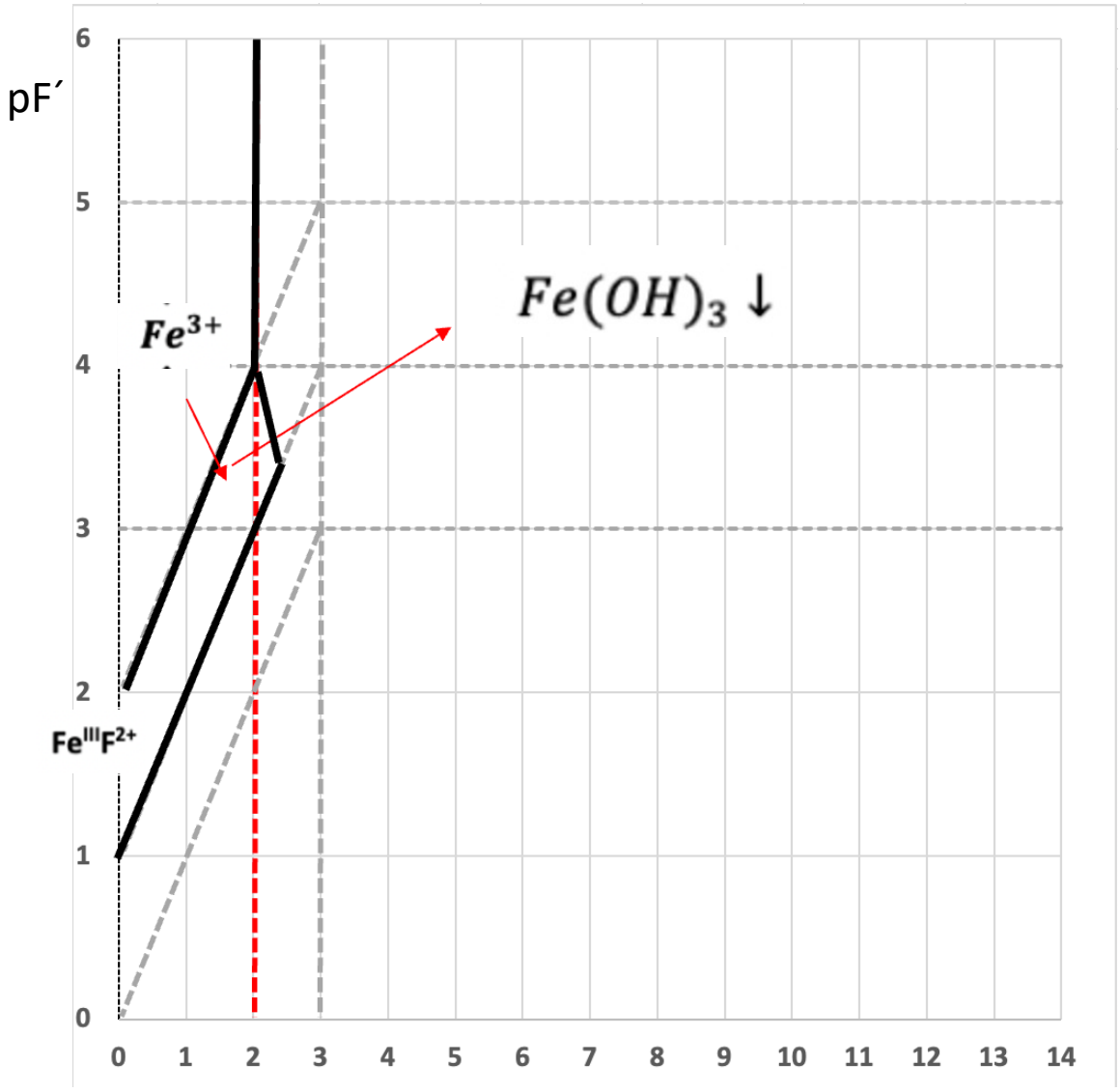
2) pKc´= f (pH):



3) Zona definitiva Fe^{3+} :



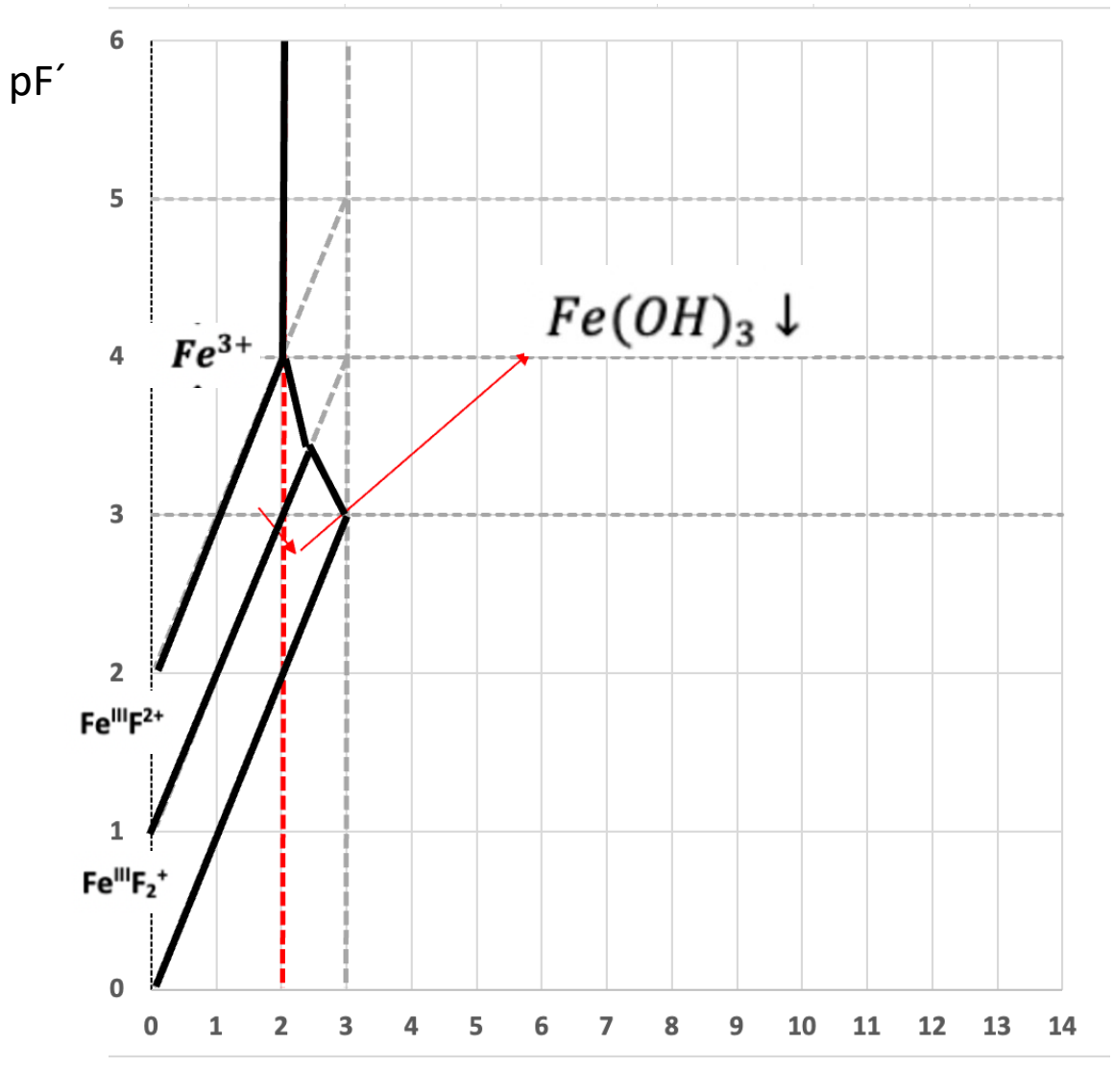
4) Zona definitiva de los complejos sucesivos :



$$Fe^{III}F^{2+} + 3H_2O \rightleftharpoons Fe(OH)_{3\downarrow} + HF + 2H^+$$

L:2H

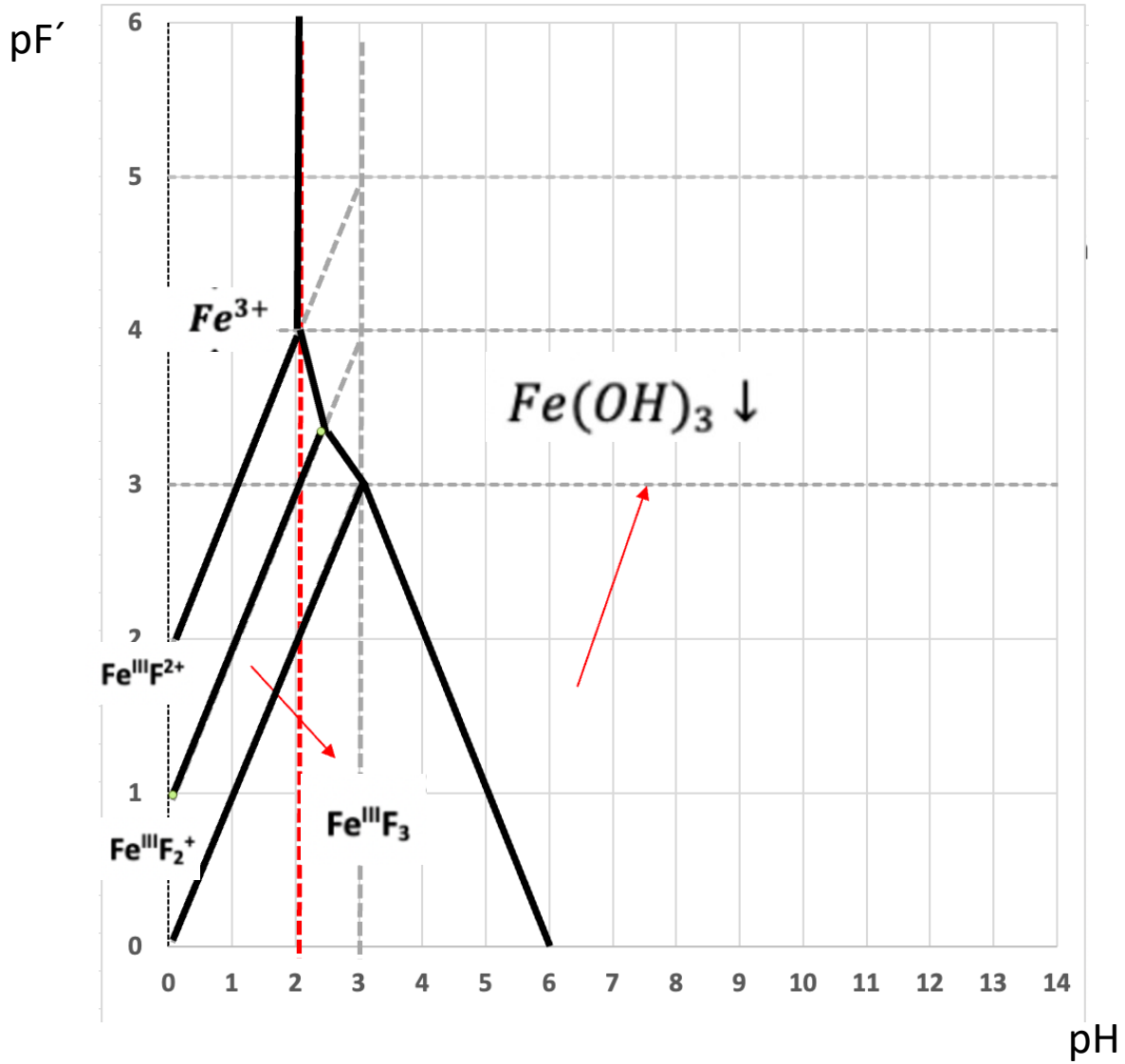
m = - 2



$$Fe^{III}F_2^{+} + 3H_2O \rightleftharpoons Fe(OH)_{3\downarrow} + 2HF + H^{+}$$

2L:1H

m = - 1/2

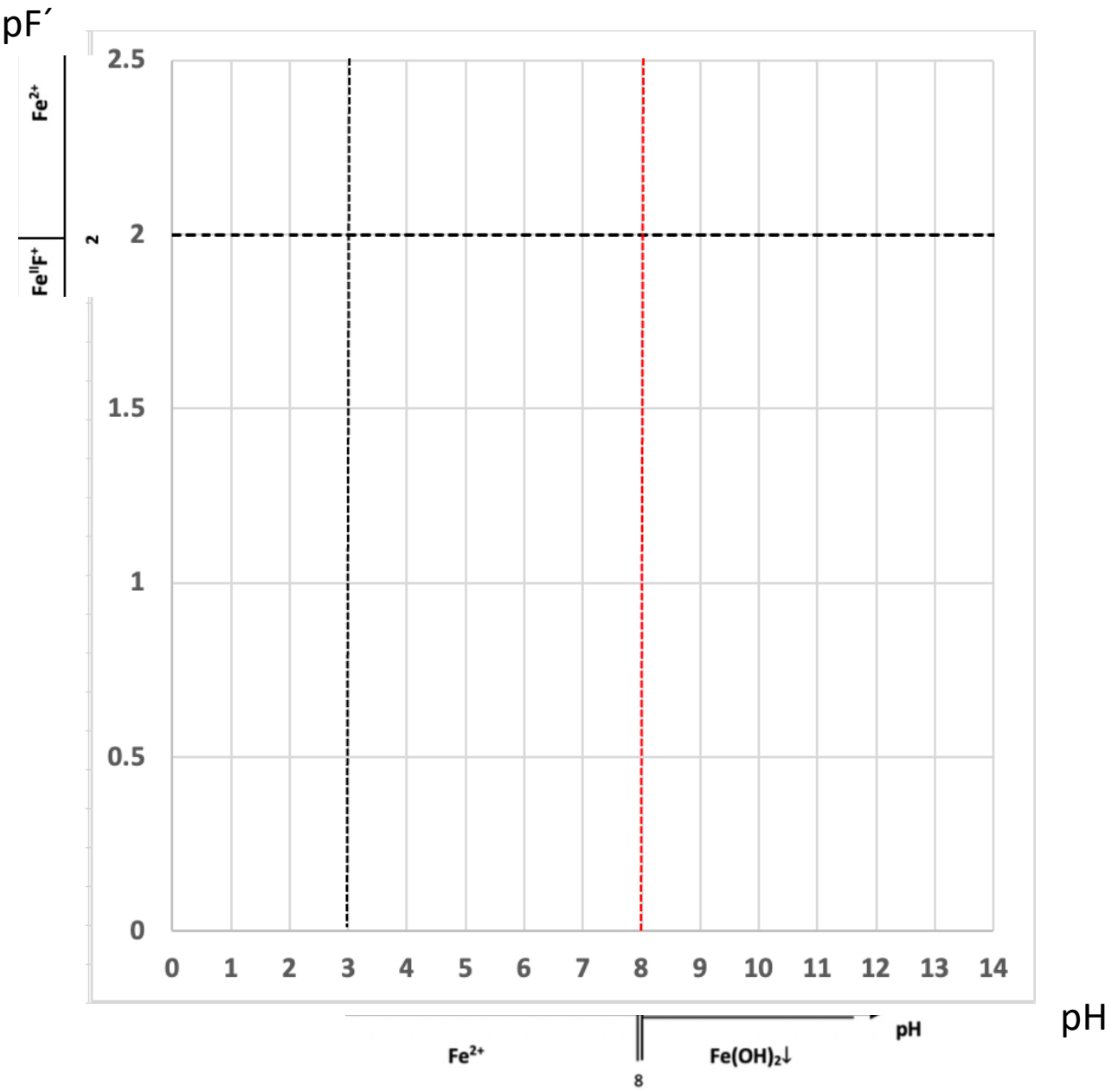


$$Fe^{III}F_3 + 3H_2O \rightleftharpoons Fe(OH)_{3\downarrow} + 3F + 3H^+$$

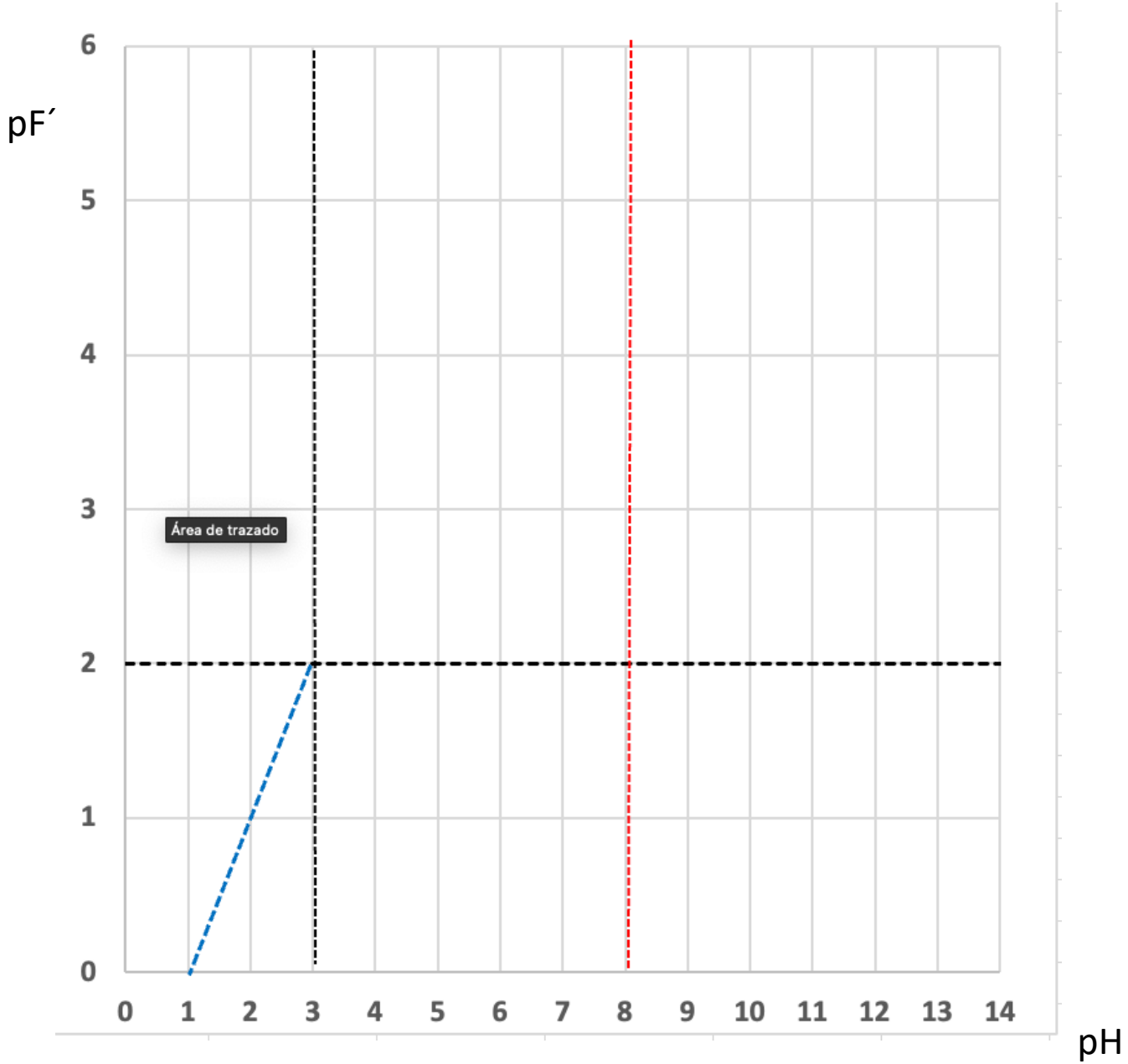
3L:3H

m = -1

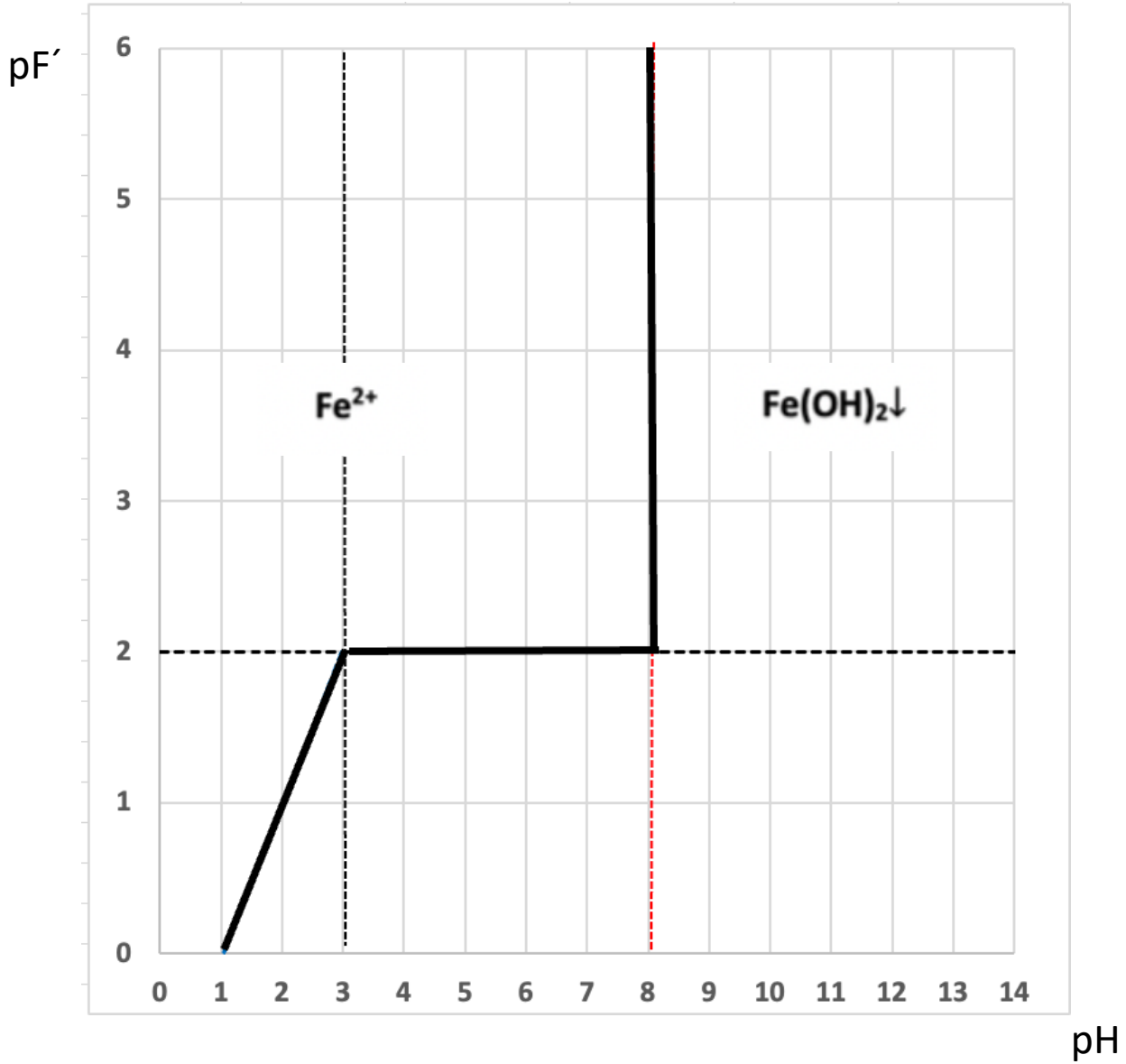
1) Guias guía Fe(II):



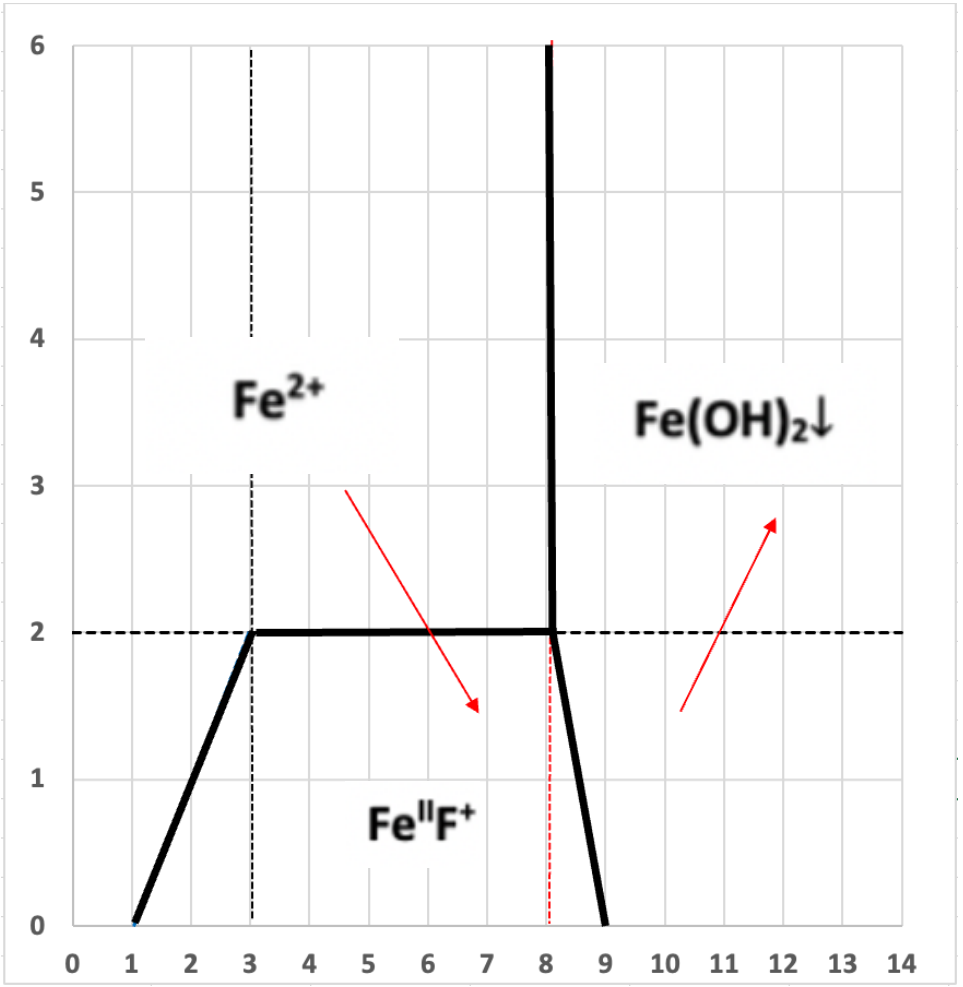
2) pKc´= f (pH):



3) Zona definitiva Fe^{2+} :



4) Zona definitiva de los complejos sucesivos :

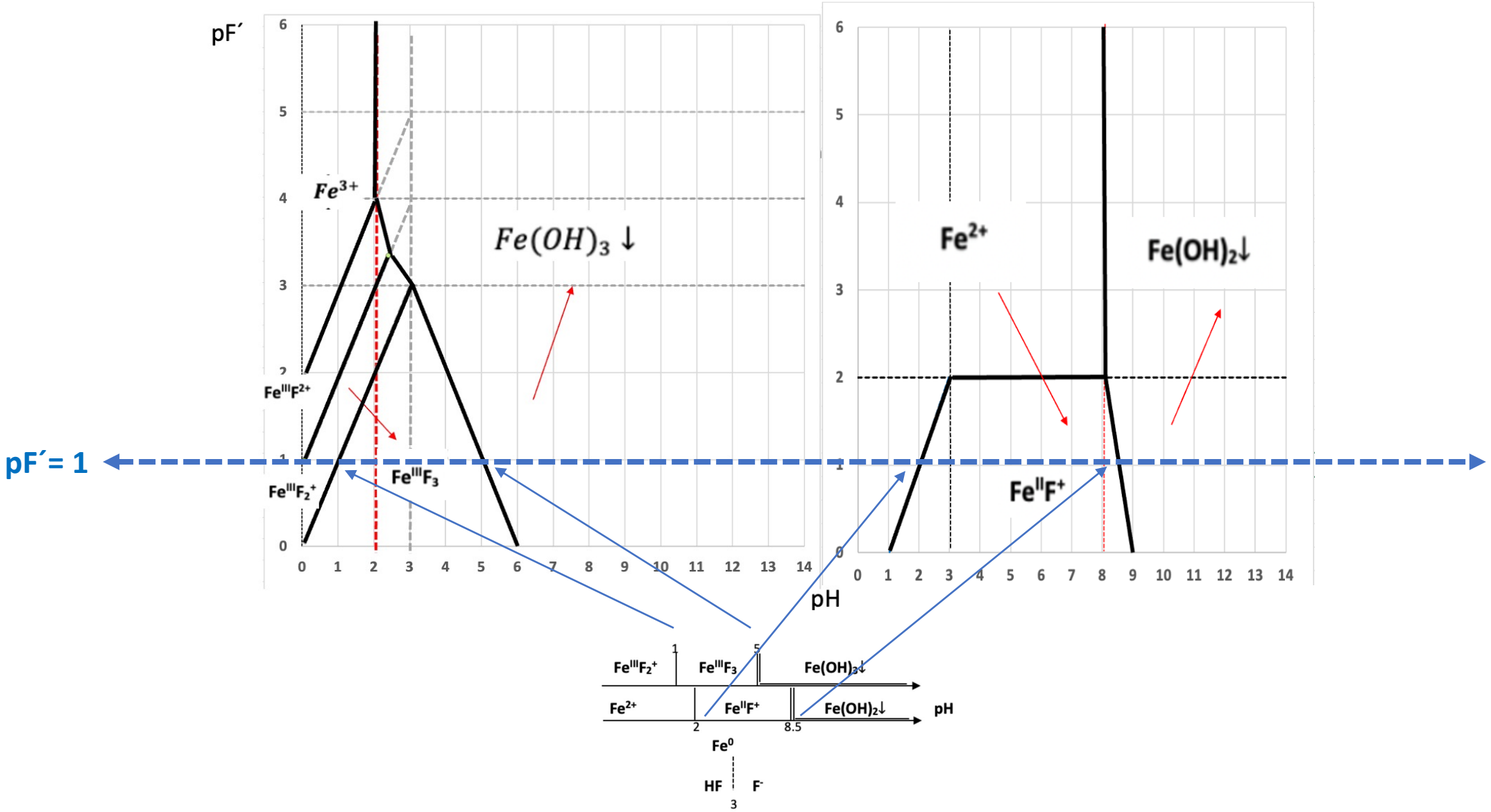


$$Fe^{II}F^{+} + 2H_2O \rightleftharpoons Fe(OH)_{2\downarrow} + F^{-} + 2H^{+}$$

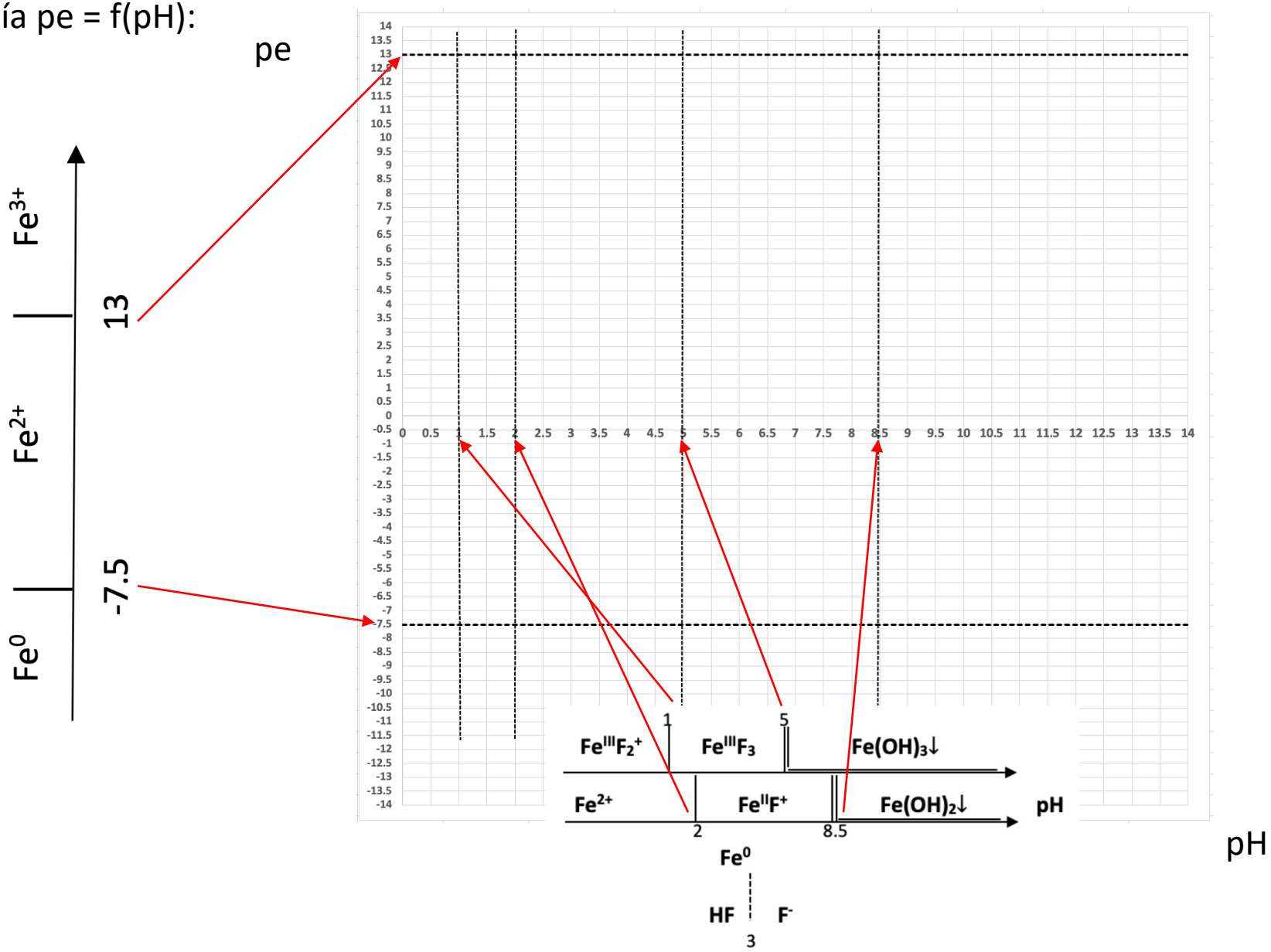
1L:2H

m = +2

DGPERedox a pF´= 1:

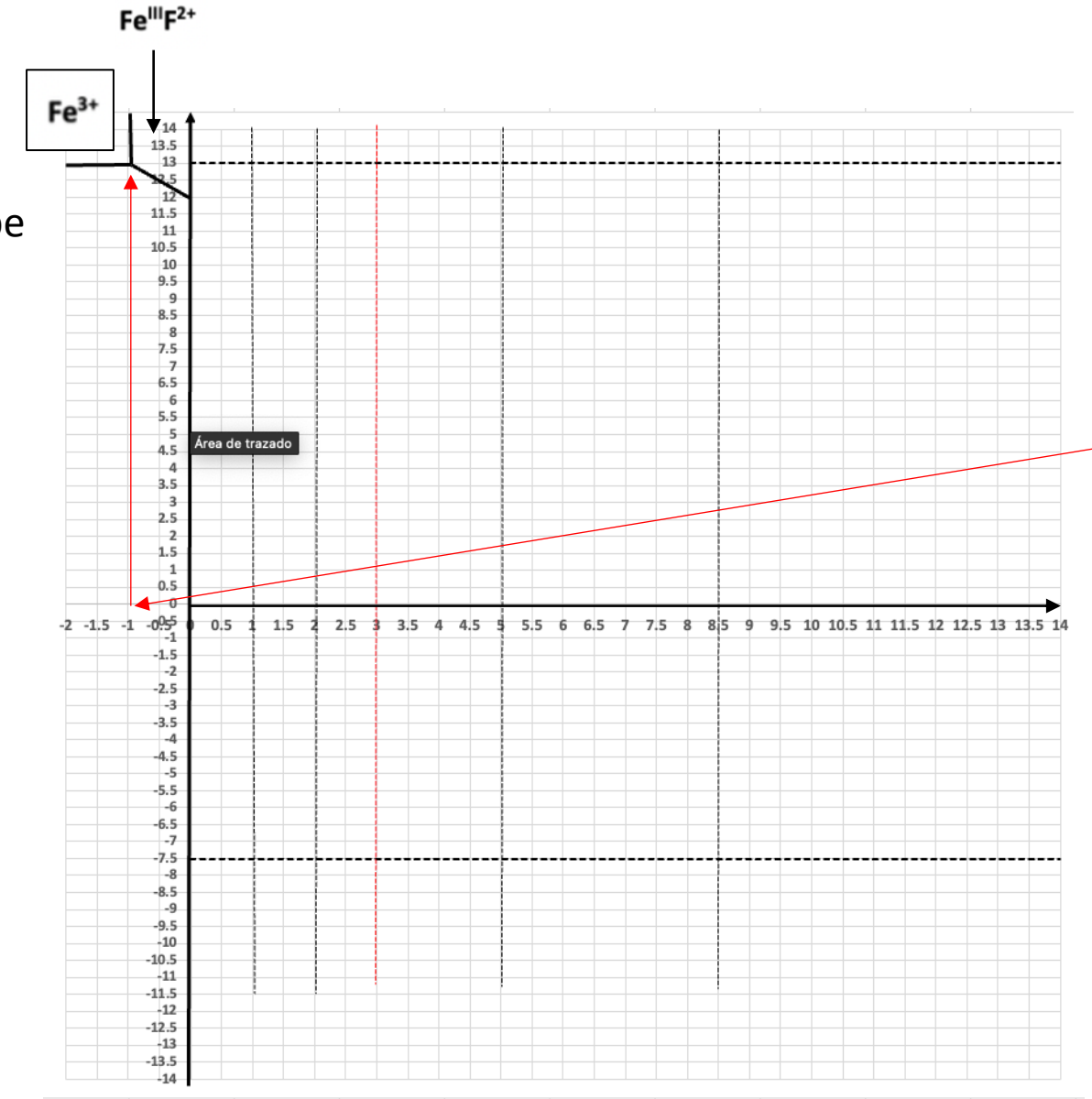


1) Lineas guía pe = f(pH):



1ro. Fe(III)/Fe(II)

1) Zona del Fe^{3+} y FeF^{2+}:



$Fe^{2+} \rightleftharpoons Fe^{3+} + 1e^-$ $\quad K_r = 10^{13}$

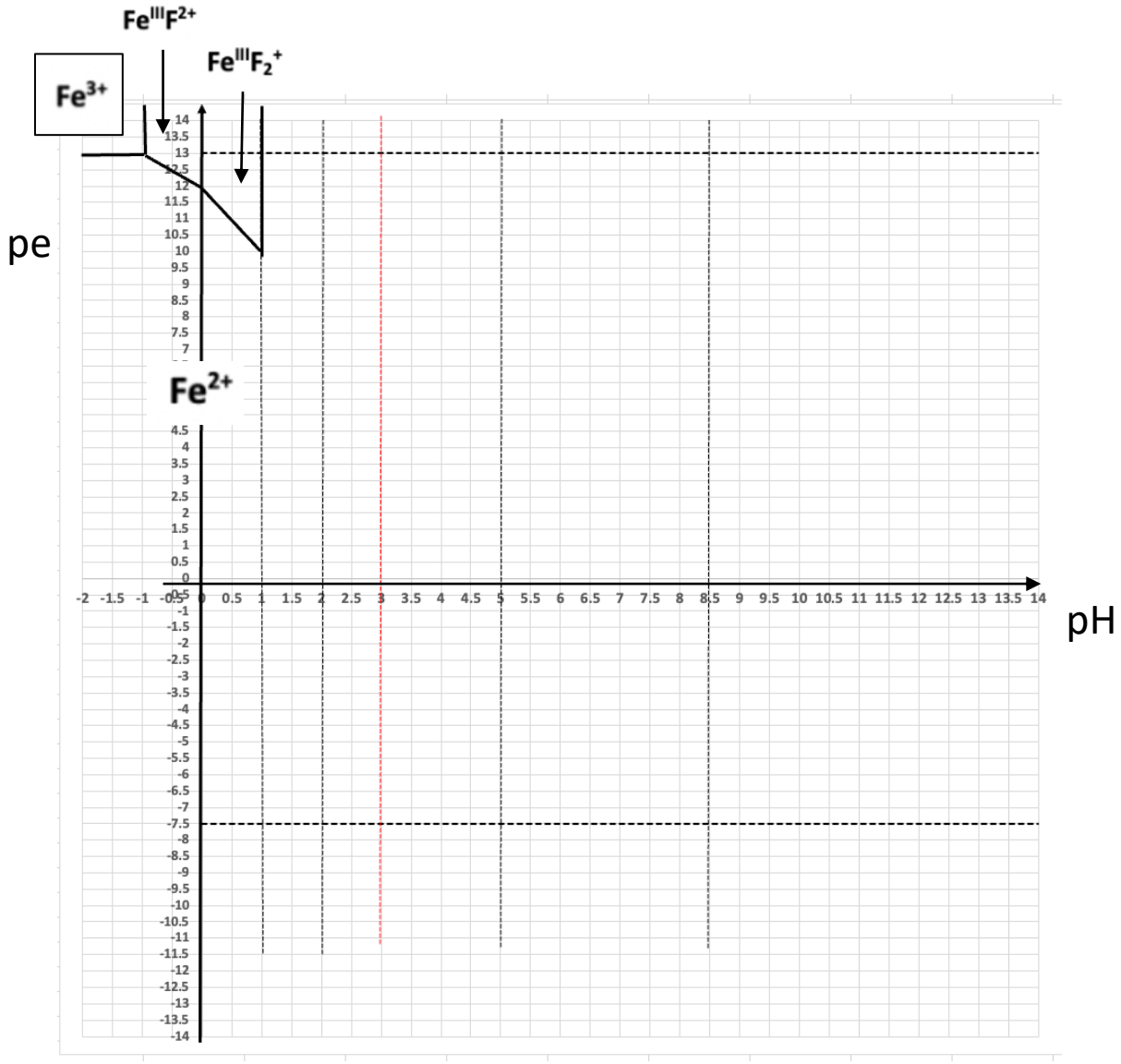
∴ pe = 13

$Fe^{2+} + HF \rightleftharpoons FeF^{2+} + 1e^- + H^+$ $\quad K_{rg}{}' = 10^{14}$

∴ pe = 14 – pH

pH_{transc} = -1: $\quad Fe^{2+} \rightarrow FeF^{2+}$

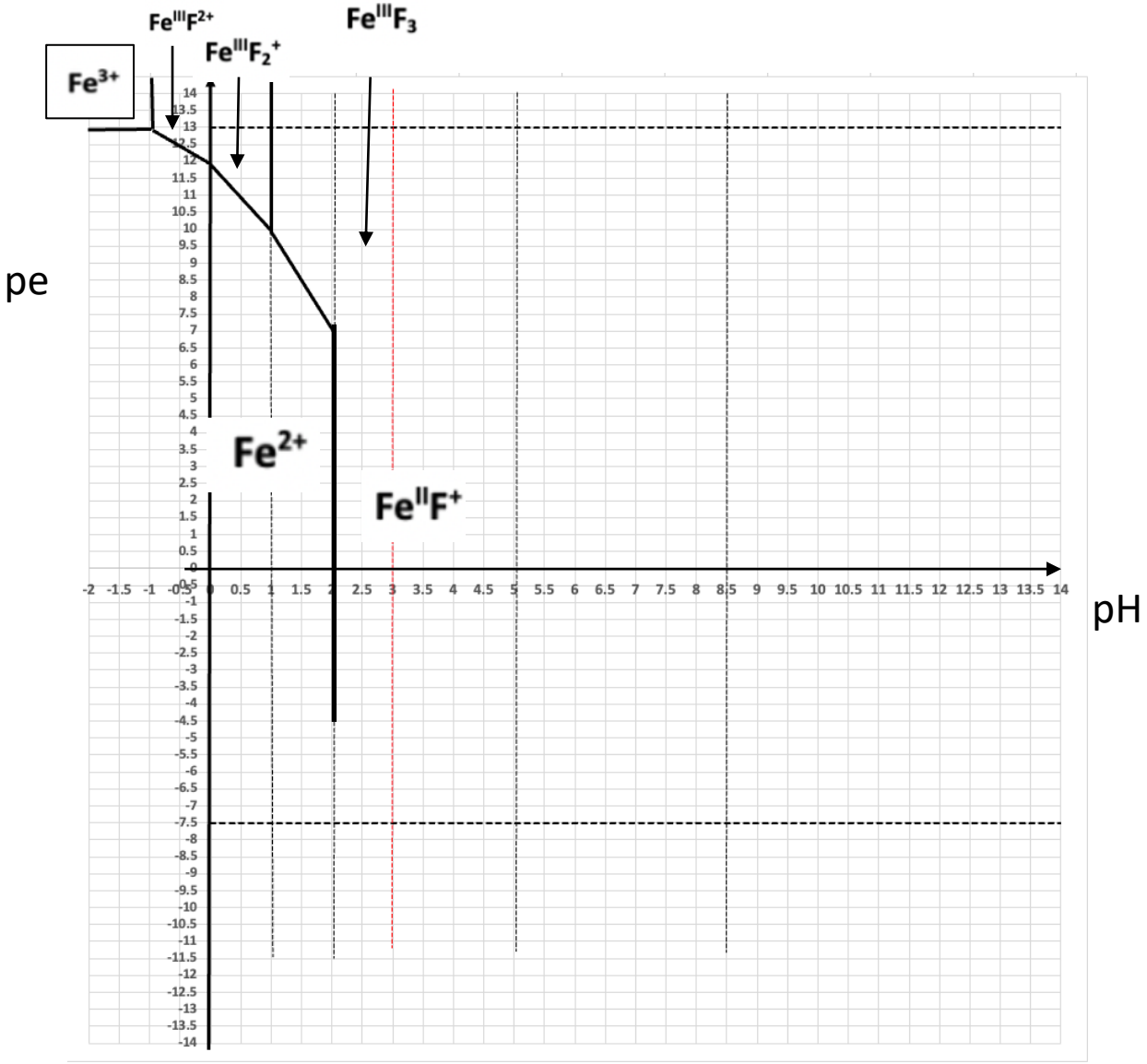
2) Siguientes complejos:



$$Fe^{2+} + 2HF \rightleftharpoons FeF_2^+ + 1e^- + 2H^+$$

1e:2H

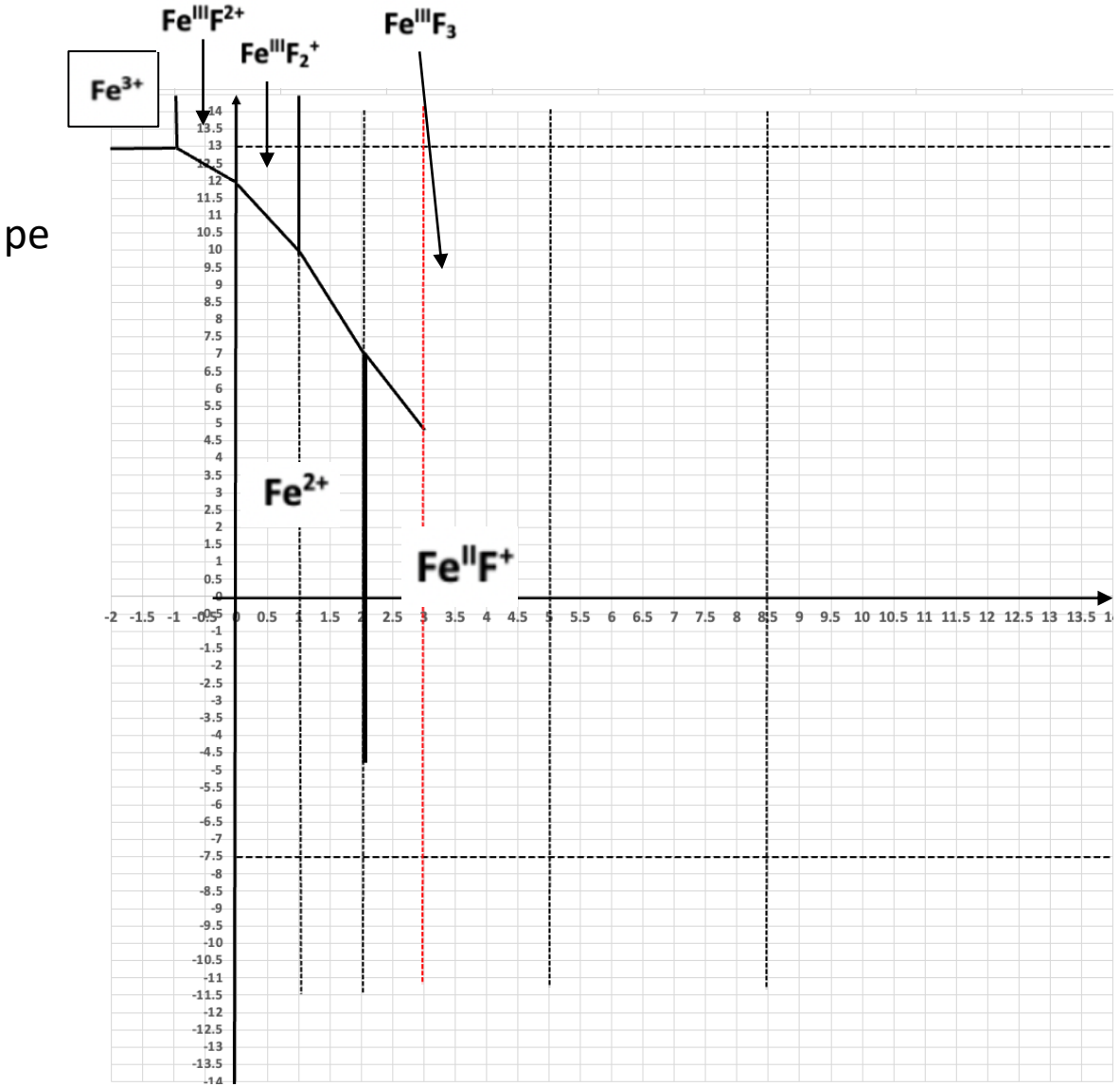
m = -2



$$Fe^{2+} + 3HF \rightleftharpoons FeF_3^0 + 1e^- + 3H^+$$

1e : 3H

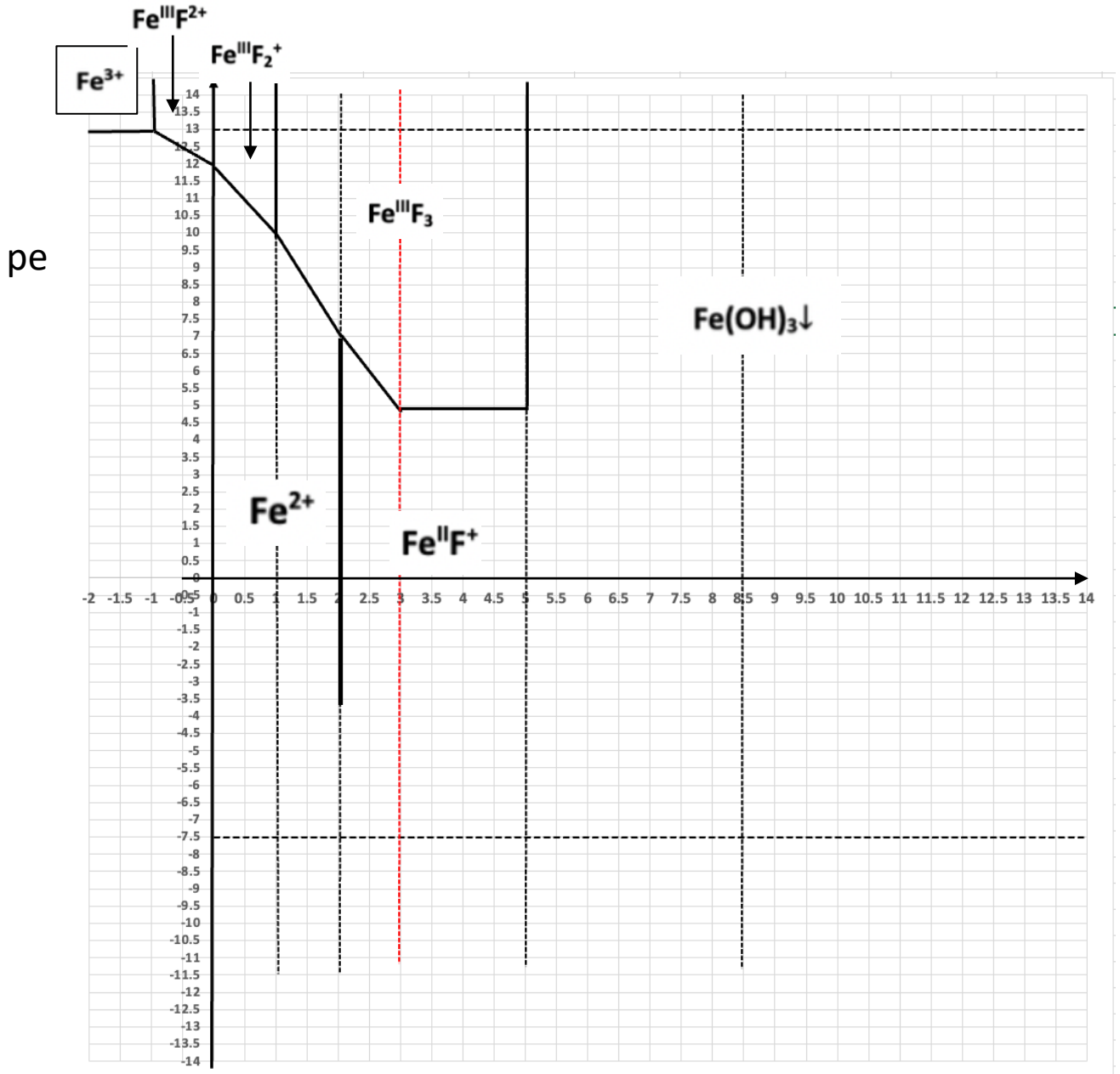
m = -3



$$FeF^{+} + 2HF \rightleftharpoons FeF_3^0 + 1e^{-} + 2H^{+}$$

1e : 2H

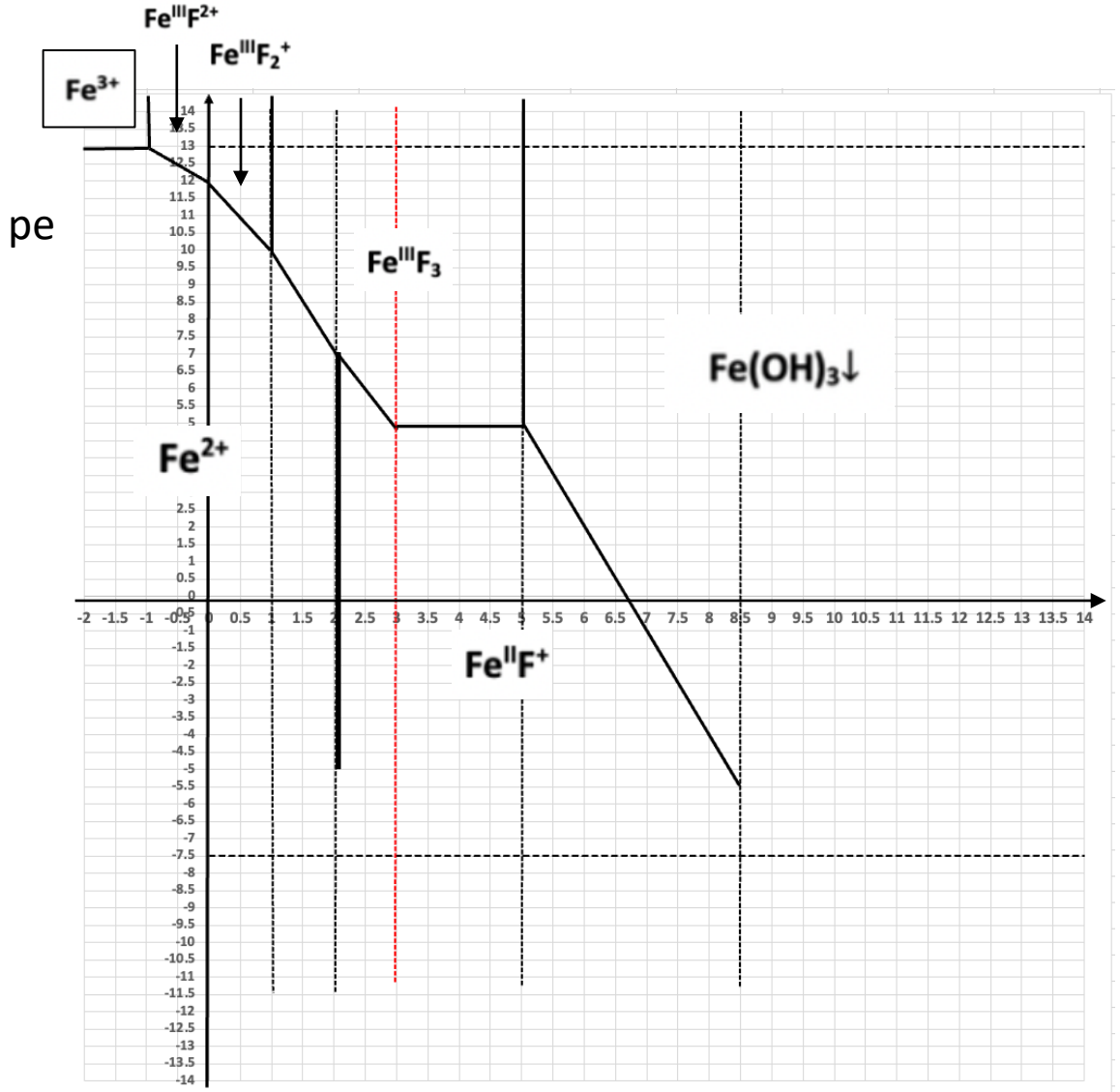
m = -2



$$FeF^{+} + 2F^{-} \rightleftharpoons FeF_3^0 + 1e^{-}$$

1 e : 0 H

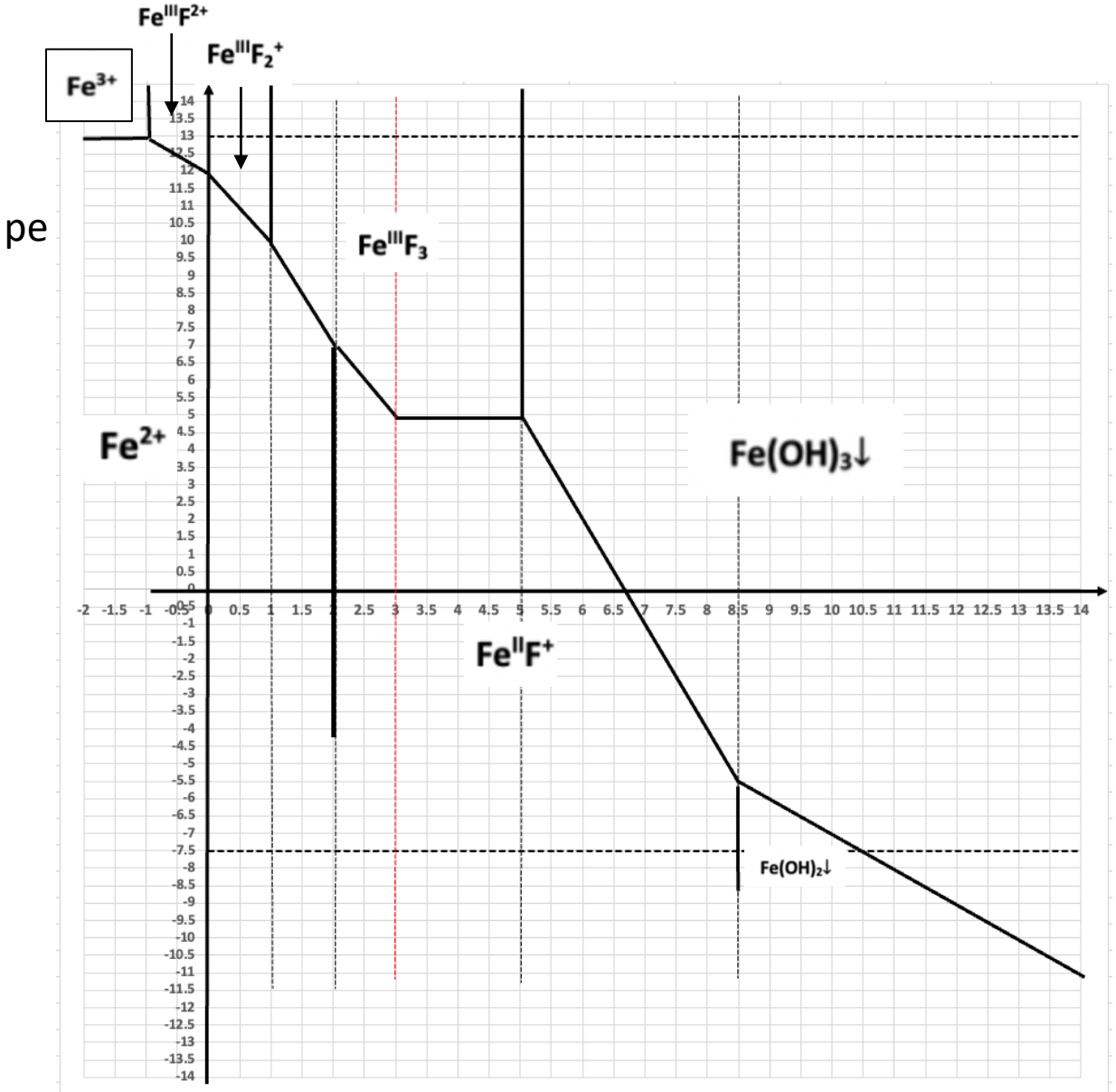
m = 0



$$FeF^{+} + 3H_2O \rightleftharpoons Fe(OH)_{3\downarrow} + 1e^{-} + 3H^{+}$$

1e = 3H

m = -3

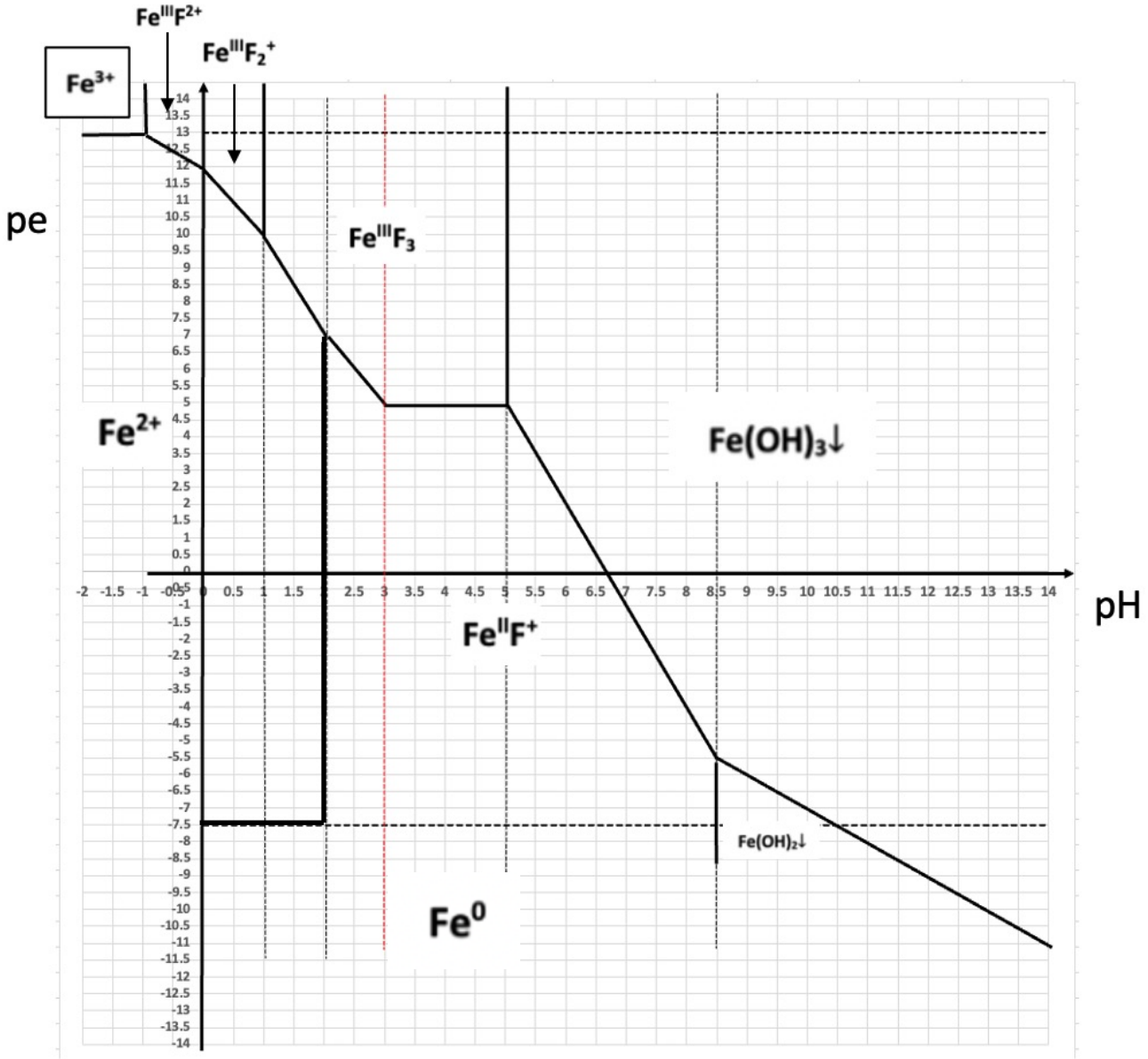


$$Fe(OH)_{2\downarrow} + H_2O \rightleftharpoons Fe(OH)_{3\downarrow} + 1e^- + H^+$$

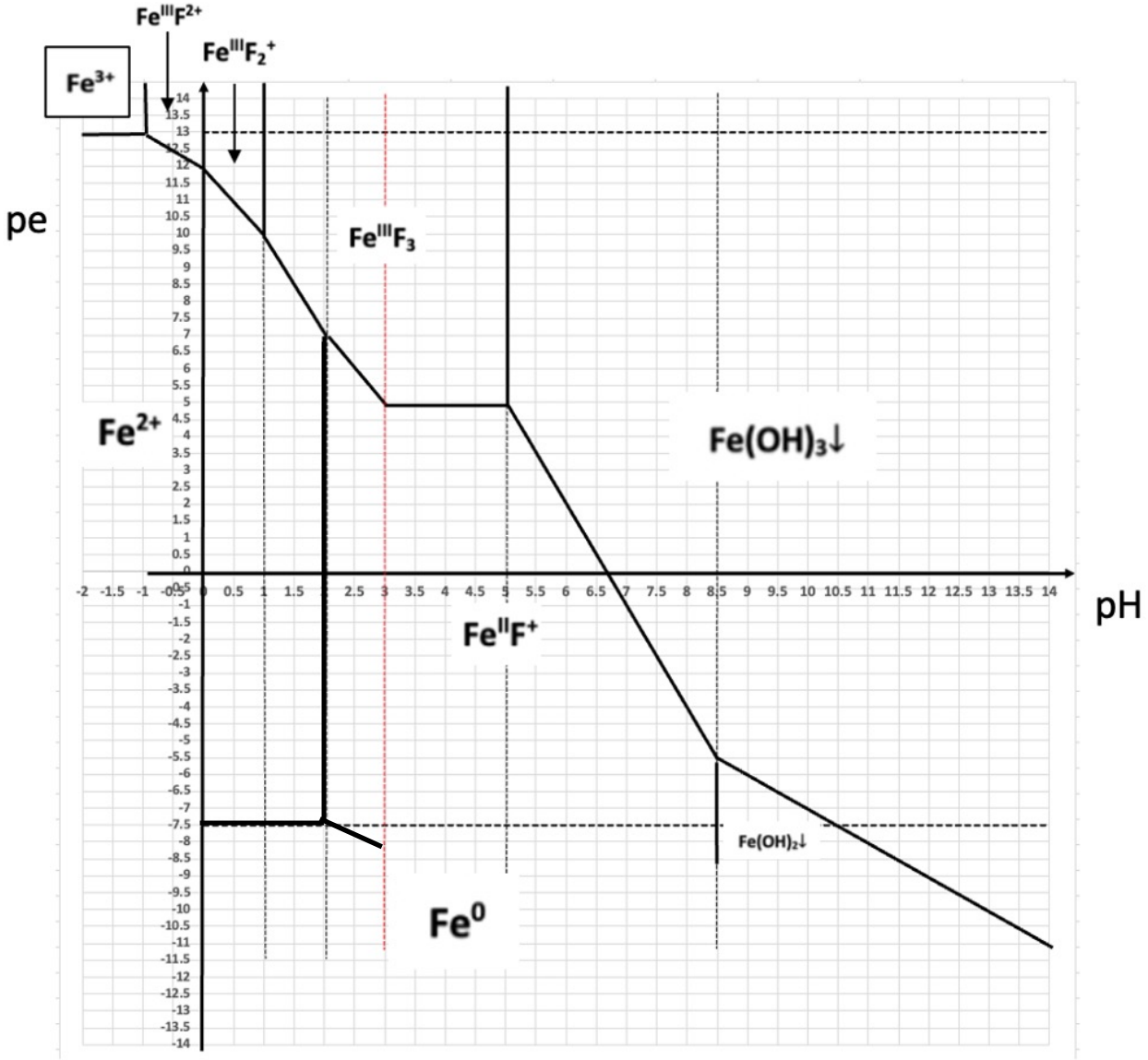
1e : 1H

M. = -1

2do. Fe(II)/Fe(0)



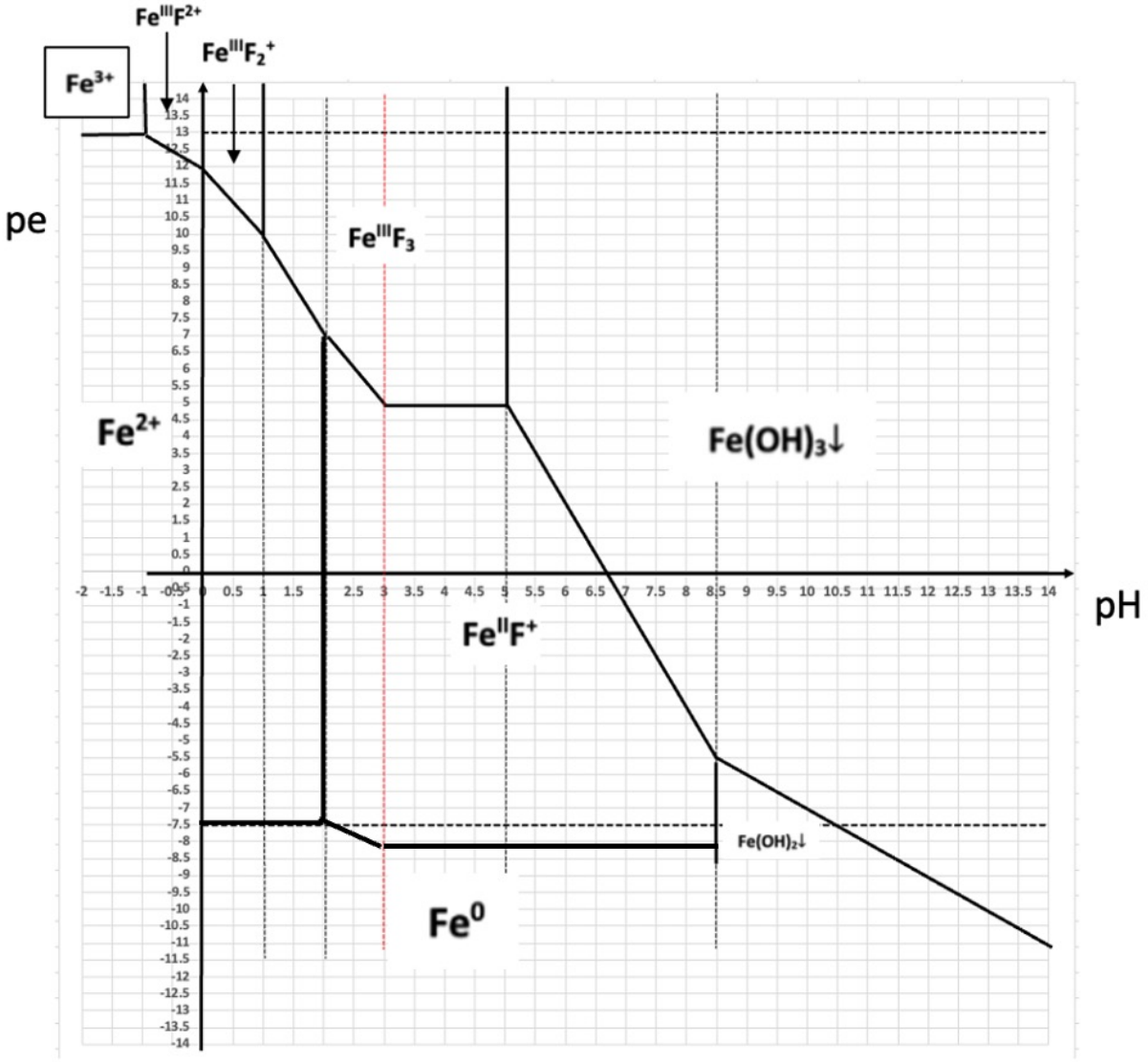
$$Fe^0 \rightleftharpoons Fe^{2+} + 2e^- \qquad K_r = 10^{-15}$$



$$Fe^0 + HF \rightleftharpoons FeF^+ + 2e^- + H^+$$

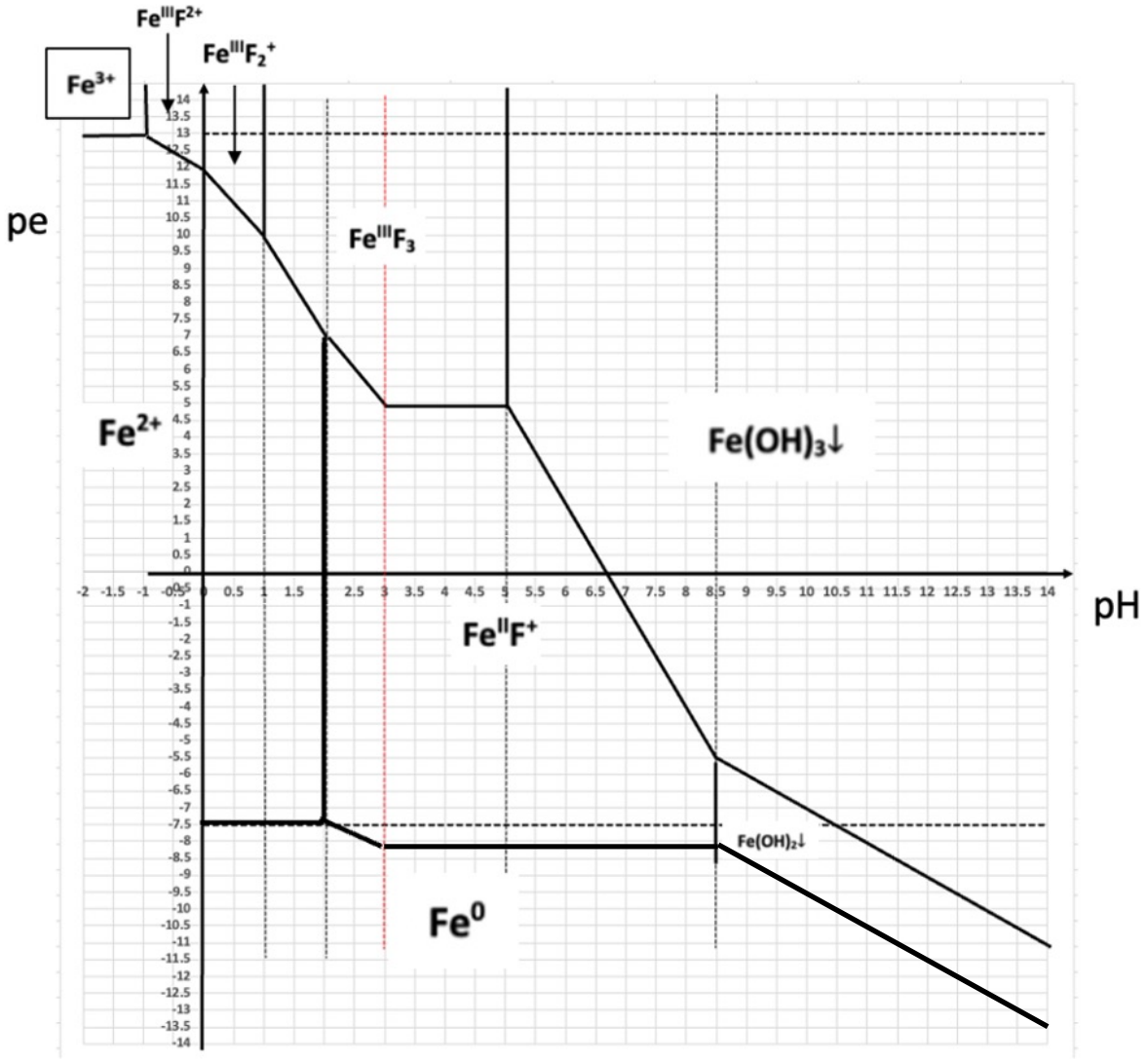
2e : 1H

m = -1/2



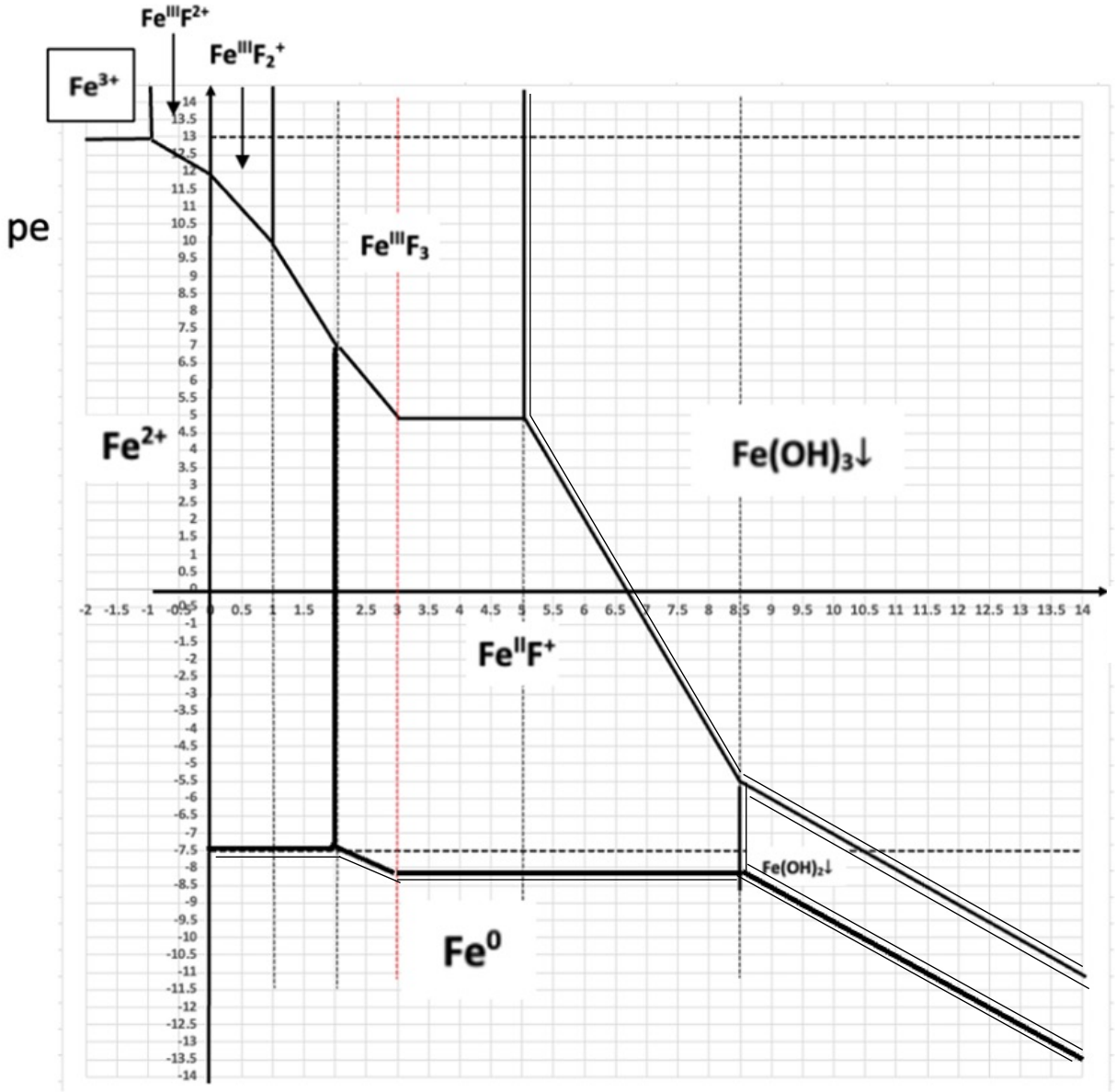
$$Fe^0 + F^- \rightleftharpoons FeF^+ + 2e^-$$

2e : 0H
m = 0



$$Fe^0 + 2H_2O \rightleftharpoons Fe(OH)_{2\downarrow} + 2e^- + 2H^+$$

1e : 1H
m = -1


Fe^{III}F^{2+}
Fe^{III}F$_2^+$
Fe^{3+}
pe
Fe^{III}F$_3$
Fe^{2+}
Fe(OH)$_3$↓
Fe^{II}F$^+$
Fe(OH)$_2$↓
Fe^0
[pH]$_{pM=2,pL=1}$