### Class problem

1a) Solid calcium fluoride ( $CaF_{2(s)}$ ) is added to pure water so that at equilibrium some solid remains dissolved. Given that the solubility product is 3 x  $10^{-11}$  M<sup>3</sup>, what is the equilibrium concentration of F<sup>-</sup> in water?

Solubility product relation: 
$$CaF_{2(s)} = Ca^{2+} + 2F^{-}$$

Since some solid remains at equilibrium, the solubility relationship must be satisfied

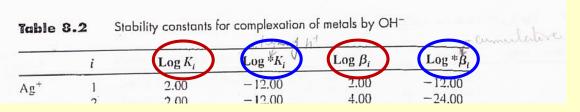
$$[Ca^{2+}][F^{-}]^{2} = 3 \times 10^{-11}$$
 (1)

Two unknowns, Ca<sup>2+</sup> and F<sup>-</sup>, and one equation?

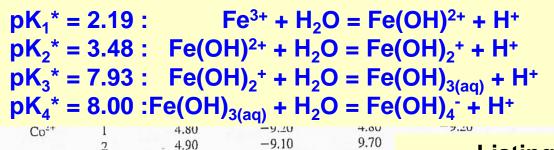
### Two options:

- use stoichiometry of dissolution
- charge balance (useful if we know all other constituents present)

## Metal-Complexation Reactions with OH-



#### Listing all reactions and constants sequentially



-12.90

-4.00

-5.62

-7.13

-11.02

-8.00

-5.68

-13.22

-12.70

-11.07

-10.43

-2.19

-3.48

-7.93

-8.00

-9.50

1.10

10.00

8.38

6.87

2.98

6.00

8.32

0.78

1.30

4.50

2.93

3.57

11.81

10.52

6.07

6.00

 $Cr^{3+}$ 

Cu2+

Fe2+

Fe3+

10.80

10.00

#### In terms of OH-

$$K_i$$
:  $Fe^{3+} + OH^- = Fe(OH)^{2+}$   
 $\beta_i$ :  $Fe^{3+} + 2OH^- = Fe(OH)_2^+$ 

#### In terms of H+

$$K_i^*$$
: Fe<sup>3+</sup> + H<sub>2</sub>O = Fe(OH)<sup>2+</sup> + H<sup>+</sup>  
 $\beta_i^*$ : Fe<sup>3+</sup> + 2H<sub>2</sub>O = Fe(OH)<sub>2</sub><sup>+</sup> + H<sup>+</sup>

## Listing all reactions and constants cumulatively (in terms of component Fe<sup>3+</sup>)

18.38  
25.25  
28.23  

$$\beta_{1}^{2} = 2.19$$
:  
 $\beta_{2}^{2} = 5.67$ :  
 $\beta_{3}^{2} = 13.6$ :  
 $\beta_{4}^{2} = 21.6$ :

## **Solubility Expressions**

### Listing all reactions and constants

```
p\beta_1^* = 2.19: Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+

p\beta_2^* = 5.67: Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+

p\beta_3^* = 13.6: Fe^{3+} + 3H_2O = Fe(OH)_{3(aq)} + 3H^+

p\beta_4^* = 21.6: Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+
```

At any state of the system,

[TOTFe<sub>diss</sub>] = [Fe<sup>3+</sup>] + [Fe(OH)<sup>2+</sup>]+ [Fe(OH)<sub>2</sub>+]+ [Fe(OH)<sub>3(aq)</sub>] + [Fe(OH)<sub>4</sub>-]  
= [Fe<sup>3+</sup>](1 + 
$$\beta_1$$
\*/[H+] +  $\beta_2$ \*/[H+]<sup>2</sup> +  $\beta_3$ \*/[H+]<sup>3</sup> +  $\beta_4$ \*/[H+]<sup>4</sup>)

# Solubility Curve for Fe(OH)<sub>3(s)</sub>

```
[TOTFe<sub>diss</sub>] = [Fe<sup>3+</sup>] + [Fe(OH)<sup>2+</sup>]+ [Fe(OH)<sub>2</sub>+]+ [Fe(OH)<sub>3(aq)</sub>] + [Fe(OH)<sub>4</sub>-]

= [Fe<sup>3+</sup>](1 + \beta_1*/[H+] + \beta_2*/[H+]<sup>2</sup> + \beta_3*/[H+]<sup>3</sup> + \beta_4*/[H+]<sup>4</sup>)
```

