Effect of Complexation on Solubility

What is the molar solubility of CaF_2 in the presence of 0.20 M Y^{4-}? The reaction that accounts for its solubility is

$$\mathrm{CaF_2}(s) + \mathrm{Y^{4-}}(aq) \rightleftharpoons \mathrm{CaY^{2-}}(aq) + 2\mathrm{F^-}(aq)$$

To find this reaction's equilibrium constant, we note that it is the sum of these two reactions

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\mathrm{F^-}(aq)$$

$$\mathrm{Ca^{2+}} + \mathrm{Y^{4-}} \rightleftharpoons \mathrm{CaY^{2-}}$$

for which the equilibrium constant is

$$K = K_{sp} \times K_1 = (3.9 \times 10^{-11})(4.9 \times 10^{10}) = 1.911$$

Trying to solve by simply letting the system move directly to equilibrium will not work when using simplifying assumptions as it yields negative concentrations; this frequently is the case when working with complexation chemistry when the initial condition is rich in reactants and deficient in products, as is the case here. To make the problem more tractable, we first let the reaction proceed to completion by using up the limiting reagent, which is EDTA and then let the system relax back to its equilibrium position; thus, we have the following ICE table.

$CaF_2(s)$	+	$Y^{4-}(aq)$	$\rightleftharpoons$	$CaY^{2-}(aq)$	+	$2F^-(aq)$
—		0.20		0		0
—		–0.20		+0.20		+0.40
—		0		0.20		0.40
—		+x		–x		–2x
—		x		0.20 – x		0.40 – 2x

$$K = \frac{[\mathrm{CaY^{2-}}][\mathrm{F^-}]^2}{[\mathrm{Y^{4-}}]} = \frac{(0.20 - x)(0.40 - 2x)^2}{x} = 1.911$$

$$\text{assume } 0.20 - x \approx 0.2 \text{ and } 0.40 - 2x \approx 0.40$$

$$K = \frac{(0.20)(0.40)^2}{x} = 1.911$$

$$x = 0.0167$$

Checking assumptions, we find that the errors

$$100 \times \frac{0.20 - (0.20 - 0.0167)}{0.20} = 8.35\%$$

are too large. For our new simplification, we assume that $0.20 - x \approx 0.1833$ and $0.40 - 2x \approx 0.3666$; this gives

$$K = \frac{(0.1833)(0.3666)^2}{x} = 1.911$$

$$x = 0.0129$$

with errors of

$$100 \times \frac{0.1833 - (0.20 - 0.0129)}{0.1833} = -2.07\%$$

Note that x is the concentration of uncomplexed Y^{4-}; we are looking for the molar solubility, which is equivalent to the concentration of CaY^{2-}, which is

$$0.20 - x = 0.20 - 0.0129 = 0.1871 \text{ M}$$

Note that this a much greater solubility for $CaF_2(s)$ than we found earlier when we considered only its solubility in water.