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REACTIONS BETWEEN CEROUS AND FLUORIDE IONS*

P. L. SARMA and M. S. DAVIS†
Department of Chemistry, University of North Dakota,
Grand Forks, North Dakota 58201

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Abstract—Gradual addition of a sodium fluoride solution to a fixed amount of a cerous nitrate solution indicated the successive formation of CeF^{2+}, CeF_2^+ and $CeF_2 \cdot CeF^{2+}$ and CeF_2^+ appeared to undergo partial hydrolysis forming $CeF(OH)^+$ and $CeF_2(OH)$, respectively. The same products appeared to be formed successively in the reverse order when the cerous nitrate solution was gradually added to a fixed amount of the sodium fluoride solution.

INTRODUCTION

CEROUS fluoride has a solubility product constant(1) of about 1×10^{-15}. It is one of the most insoluble fluorides.(2) However, on adding a cerous nitrate solution to a sodium fluoride solution, one of us (P. L. S.) observed that the precipitate first formed redissolved on the addition of more cerous nitrate solution. Thus, the formation of some complex or complexes was suggested.

KUREY *et al.*(3) assumed that, in the reaction between cerous and fluoride ions, one of the products formed was CeF^{2+}. A solution containing this ion showed no Tyndall effect. However in Sarma's observation, the dissolution of cerous fluoride with a cerous nitrate solution was preceded by the appearance of a slightly gelatinous precipitate. This could not be explained by the formation of CeF^{2+} alone. Furthermore, Kury and co-workers thought that there might be more than one complex when cerous and fluoride ions reacted with each other. Therefore, in this work, the complexes formed by cerous and fluoride ions were investigated using potentiometric and nephelometric methods.

EXPERIMENTAL

Reagent grade sodium fluoride (CB 721: Matheson Coleman and Bell) was used to prepare a 0·6000 M solution of sodium fluoride. It was stocked in a polyethylene bottle. Another stock solution of 0·1000 M cerous nitrate solution was prepared from $Ce(NO_3)_3 \cdot 6H_2O$ of 99·9+ per cent purity (Code No. 277: American Potash and Chemical Corporation, West Chicago, Illinois, U.S.A.). Before making the second stock solution, cerous nitrate was further purified by recrystallizing twice from triple distilled water. Any possible trace of nitric acid in cerous nitrate was thus removed. Other solutions of sodium fluoride and of cerous nitrate were prepared by diluting portions of these two stock solutions. Triple distilled water, cooled in an atmosphere of nitrogen, was used throughout this work. Before mixing the solutions, the pH of each solution was adjusted to 5·750 with nitric acid. The possibility of more than one reaction due to differences in the pH of the solutions was thus

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[†] Present address: North Iowa Area Community College, Mason City, Iowa 50401.

(1) J. L. WEAVER and W. C. PURDY, *Analytica chim. Acta* **20,** 376 (1959).

(2) J. H. REEDY, *Theoretical Qualitative Analysis*, p. 408. McGraw-Hill, New York (1938).

(3) J. W. KURY, Z. Z. HUGUS and W. M. LATIMER, *J. phys. Chem.* **61,** 1021 (1957).

eliminated. A pH of 5·750 was selected as a matter of convenience: the cerous nitrate solution used in the potentiometric 'titration' (Fig. 1) had this pH value.

Dissolution of sodium fluoride in water increases the pH of water due to the hydrolysis of the salt. For the same reason, dissolution of cerous nitrate in water decreases its pH. Because these pH changes could be easily measured with a pH meter that is capable of reading down to the third decimal place, the reactions between cerous and fluoride ions were studied with potentiometric 'titrations'. Since the products of the reactions would be diluted to different concentrations at different states of titration, the common technique of potentiometric titration, where the titrant is added in portions to a fixed volume of the other solution, was not employed in this work. Instead, the same volume of one of the solutions was taken in different containers and to each container varying amounts of the 'titrant' were added. After adding water to each container until the total volume was the same in all containers, the contents were stirred under an atmosphere of nitrogen and the pH values were measured at the end of 2 min following their mixing. A Beckman Model 76 Expanded Scale pH meter with a Beckman No. 41263 general purpose glass electrode and a Beckman No. 39170 fibre junction calomel electrode was used to measure all the pH values.

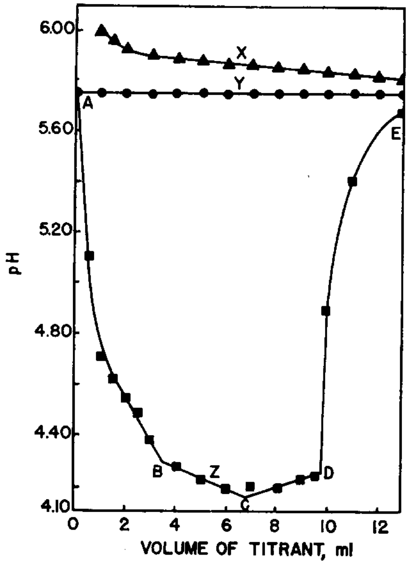

FIG. 1.—Potentiometric 'titration' of a cerous nitrate solution with a sodium fluoride solution. In Y the 'titrant' was water, and in X and Z it was a 0·06000 M sodium fluoride solution. The volume of the 'titrant' corresponding to each plot was mixed with the other solution or water or both until the total volume was 35·00 ml. Only water was mixed with varying amounts of a 0·06000 M sodium fluoride solution in X and with 20·00 ml of a 0·01000 M cerous nitrate solution in Y. In Z, different volumes of a 0·06000 M sodium fluoride solution, indicated along the X-axis, were mixed with 20·00 ml of a 0·01000 M cerous nitrate solution and water.

Separate containers were used also to mix sodium fluoride and cerous nitrate solutions for nephelometric studies. The powers of nephelometric scattering of the mixed solutions were measured with a Coleman Model 14 spectrophotometer at the end of 5 min since their mixing.

RESULTS AND DISCUSSION

The triple distilled water used in this work had a pH of 6·952. When cerous nitrate was dissolved in this water to make a 5·174 mM solution, the pH dropped to 5·750. If the reaction causing this pH drop were $Ce^{3+} + H_2O \rightleftharpoons Ce(OH)^{2+} + H^+$, the hydrolysis constant at room temperature would be 5×10^{-10}. The previously reported⁽⁴⁾ value was 1×10^{-9}.

The rare earth elements form appreciably stable complexes only when most strongly chelating ligands are used and, in particular, when these ligands contain highly electronegative donor atoms such as oxygen.⁽⁵⁾ It is also known that in aqueous solutions the fluoride ion is a very poor ligand for the transition elements; but from the results of this work it appeared that when a fixed amount of cerous ion reacted with varying amounts of fluoride ion, the latter could combine with the inner transition element, cerium, forming consecutively two complexes before forming CeF_3.

Within the range A to B (Fig. 1), the solution was free from any turbidity or precipitation. This range corresponded to the formation of the CeF^{2+} complex by ion-pair association of Ce^{3+} and F^- ions. The existence of this and similar halogen complexes of cerium was reported earlier in the literature.⁽⁵⁾ However, it appeared that their hydrolysis was not known, nor suspected, previously.

From B to C (Fig. 1), a slightly gelatinous precipitate appeared. The formation of the CeF_2^+ complex within this range was indicated. It is believed that the existence of this and similar halogen complexes of cerium, or of other inner transition elements, is not reported in the literature.

Beyond point C, a precipitate settled down and the supernatant liquid cleared away completely at and beyond point D. The range C to D corresponded to the formation of CeF_3.

An explanation of the pH changes from A to D is complicated by competing equilibria; but the following reactions were assumed to take place:

$$Ce^{3+} + F^- \rightleftharpoons CeF^{2+} \quad (1)$$
$$F^- + H_2O \rightleftharpoons HF + OH^- \quad (2)$$
$$Ce^{3+} + H_2O \rightleftharpoons Ce(OH)^{2+} + H^+ \quad (3)$$
$$CeF^{2+} + H_2O \rightleftharpoons CeF(OH)^+ + H^+ \quad (4)$$
$$CeF^{2+} + F^- \rightleftharpoons CeF_2^+ \quad (5)$$
$$CeF_2^+ + H_2O \rightleftharpoons CeF_2(OH) + H^+ \quad (6)$$
$$CeF_2^+ + F^- \rightleftharpoons CeF_3 \quad (7)$$

Because Reaction (1) has an equilibrium constant⁽⁶⁾ of 10^4, it might be assumed to go considerably to the right. Therefore, the formation of CeF^{2+} between A and B by this reaction would shift the equilibria of reactions (2) and (3) to the left. The effect would be to lower the pH by the equilibrium shift in the hydrolysis reaction of the fluoride ion and to raise it by the equilibrium shift in the hydrolysis reaction of the cerous ion. However, only a small, net pH drop is expected because of these shifts in equilibria. Therefore, it was assumed that CeF^{2+} hydrolysed according to Equation (4). If this was so, the hydrolysis constant would be 3×10^{-7}.

Between B and C, Reaction (5) was assumed to take place. Such a reaction would shift the equilibrium to the left in Reaction (2) and to the right in the Reaction (1).

⁽⁴⁾ M. J. Sienko and R. A. Plane, *Physical Inorganic Chemistry*, p. 124. W. A. Benjamin, New York (1963).

⁽⁵⁾ T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel and W. J. Randall, *Chem. Rev.* **65**, 1 (1965).

⁽⁶⁾ L. G. Sillen and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, p. 258. The Chemical Society, London (1964).

A drop in pH within this range might be due to these shifts in equilibria; but to explain the appearance of a slightly gelatinous precipitate within this same range it was assumed that the ion CeF$_2^+$ reacted with water according to Equation (6). If this was so, the results would indicate a hydrolysis constant of about 4×10^{-10}.

It was assumed that between C and D Reaction (7) took place. Since the solubility of cerous fluoride is very low, this reaction would be virtually complete. This would affect the equilibria in Reactions (2–6).

The results with nephelometric studies (Fig. 2) agreed with those of potentiometric titrations. However, an explanation of the nephelometric results is difficult, since the scattering power is dependent upon the wavelength of the incident radiations and upon the number and size of the particles formed.

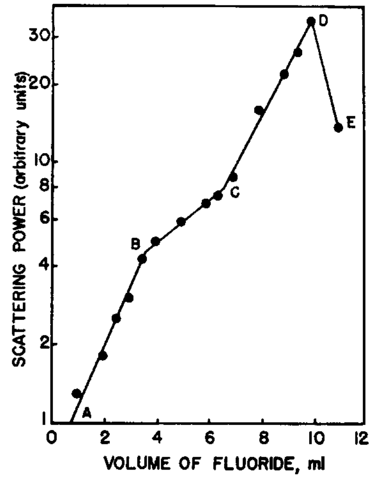

FIG. 2.—Nephelometric scattering by mixtures of cerous nitrate and sodium fluoride solutions, reference water. The volume of a 0·06000 M sodium fluoride solution, as indicated by each plot, was mixed with 20·00 ml of a 0·01000 M cerous nitrate solution and water to make a total volume of 35·00 ml.

In Figs. 3 and 4, successive formations of CeF$_3$, CeF$_2^+$ and CeF^{2+} were indicated when a fixed amount of a sodium fluoride solution reacted with varying amounts of a cerous nitrate solution. The range between A and B indicated the formation of CeF$_3$, between B and C of CeF$_2^+$, and between C and D of CeF^{2+}. It was assumed that CeF$_2^+$ and CeF^{2+} were formed according to the equations: $2CeF_3 + Ce^{3+} \rightleftharpoons 3CeF_2^+$, and $CeF_2^+ + Ce^{3+} \rightleftharpoons 2CeF^{2+}$, respectively. Changes beyond D were attributed to the dilution effects.

In Fig. 4, the inflexion point at B indicated a reaction between 3·8 m-mole of fluoride ion and 1·0 m-mole of cerous ion. This large error was caused by the coagulation of the particles and the rapid sedimentation of the precipitate during the measurements.

The known halogen complexes of the rare earths, Ln, are(5) LnF^{2+}, LnCl^{2+}, LnBr^{2+}, LnI^{2+}, LnCl$_2^+$, and LnBr$_2^+$. However, in both Figs. 3 and 4, the inflexion point at C was more pronounced than the inflexion point at D. Therefore, these results provided at least as much evidence for the formation of the CeF$_2^+$ complex as for the CeF^{2+} complex.

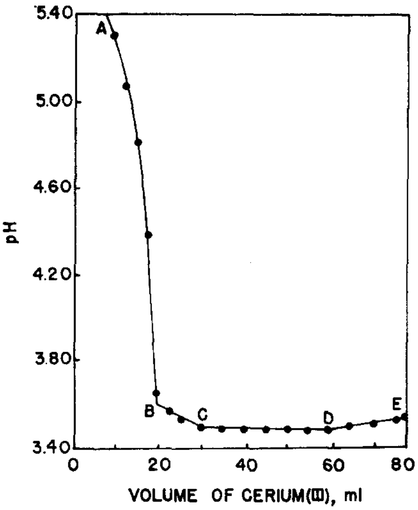

FIG. 3.—Potentiometric 'titration' of a sodium fluoride solution with a cerous nitrate solution. The volume of a 0·01000 M cerous nitrate solution that corresponded to each plot was mixed with 10·00 ml of a 0·06000 M sodium fluoride solution and water to make a total volume of 100·00 ml.

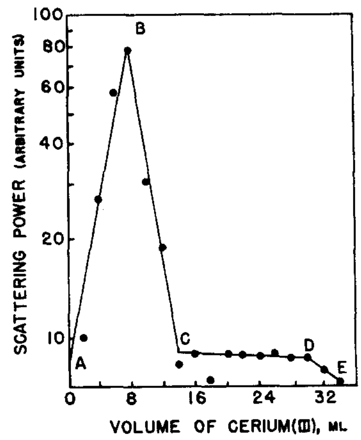

FIG. 4.—Nephelometric scattering by mixtures of sodium fluoride and cerous nitrate solutions, reference water. The volume of a 0·01000 M cerous nitrate solution, as indicated by each plot, was mixed with 5·00 ml of a 0·06000 M sodium fluoride solution and water to make a total volume of 50·00 ml.

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APPENDIX

Calculation of hydrolysis constants involved in the potentiometric titration shown in Fig. 1

I. *Determination of hydrolysis constant for cerous nitrate,* 0·005714 *M solution of* Ce^{3+} *ions.* Equilibrium expression for $Ce^{3+} + H_2O = CeOH^{2+} + H^+$:

$$K_e = \frac{(CeOH^{2+})(H^+)^*}{(Ce^{3+})(H_2O)}\,.$$

Since (H_2O) is constant:

$$K_h = \frac{(CeOH^{2+})(H^+)}{(Ce^{3+})}.$$

Determination of ($CeOH^{2+}$) in solution by the observed change in pH upon the addition of $Ce(NO_3)_3$ to the distilled water.

($CeOH^{2+}$) = $\Delta(H_1^+)$ = change in (H^+) corresponding to a change in pH produced by the addition of 0·005714 mole of $Ce(NO_3)_3$ to 1 l. of distilled water at pH 6·952.

$$\begin{aligned}(CeOH^{2+}) &= (H^+) \text{ at pH } 5{\cdot}750 - (H^+) \text{ at pH } 6{\cdot}952\\ &= -\text{anti log } 5{\cdot}750 - (-\text{ anti log } 6{\cdot}952)\\ &= 1{\cdot}778 \times 10^{-6} - 1{\cdot}117 \times 10^{-7}\\ &= 1{\cdot}66 \times 10^{-6} \text{ mole per l.}\\ &= 5{\cdot}8 \times 10^{-8} \text{ mole/35·00 ml of solution.}\end{aligned}$$

Determination of the final concentration of Ce^{3+} left in solution after formation of the complex;

final (Ce^{3+}) = initial (Ce^{3+}) − (complex)

$$= \frac{\text{M of } Ce^{3+} \text{ solution (No. of ml)}}{\text{No. of ml of total solution}} - (CeOH^{2+})$$

$$= \frac{(0{\cdot}01000)(20{\cdot}00)}{35{\cdot}00} - 1{\cdot}666 \times 10^{-6}$$

$$= 5{\cdot}712 \times 10^{-3} \text{ mole per l.}$$

Calculation of K_h for Ce^{3+}:

$$K_h = \frac{(CeOH^{2+})(H^+) \text{ at pH } 5{\cdot}750}{\text{final } (Ce^{3+})} = \frac{1{\cdot}666 \times 10^{-6}(1{\cdot}778 \times 10^{-6})}{5{\cdot}712 \times 10^{-3}}$$

$$= 5{\cdot}186 \times 10^{-10}.$$

II. *Determination of* (HF) *in fluoride solution at pH* 5·750 *for the reaction* $F^- + H_2O = HF + OH^-$.

$$(HF) = \frac{K_h(F^-)}{(OH^-)}.$$

Determination of K_h for HF:

$$K_h = \frac{K_w}{K_a}.$$

$$= \frac{1{\cdot}0 \times 10^{-14}}{7{\cdot}2 \times 10^{-4}}$$

$$= 1{\cdot}4 \times 10^{-11}.$$

Determination of (OH^-) at pH 5·750:

$$(OH^-) = \frac{1{\cdot}0 \times 10^{-14}}{(H^+) \text{ at pH } 5{\cdot}750}$$

$$= \frac{1{\cdot}0 \times 10^{-14}}{1{\cdot}8 \times 10^{-6}}$$

$$= 5{\cdot}6 \times 10^{-9}.$$

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* ( ) Stands for concentration.

Determination of (HF) in fluoride solution at pH 5·750:

$$(\mathrm{HF}) = \frac{K_h(\mathrm{F}^-)\text{ in original }0{\cdot}0600\text{ M fluoride solution}}{(\mathrm{OH}^-)}$$

$$= \frac{1{\cdot}4 \times 10^{-11}(6{\cdot}0 \times 10^{-2})}{5{\cdot}6 \times 10^{-9}}$$

$= 1{\cdot}5 \times 10^{-4}$ mole per l.

$= 5{\cdot}0 \times 10^{-7}$ mole per 3·33 ml of fluoride solution.

III. *Calculation of hydrolysis constant for* $\mathrm{CeF^{2+}}$, *assuming the reaction* $\mathrm{CeF^{2+} + H_2O = CeFOH^+ + H^+}$ (*point A to point B, Fig.* 1).

$$K_h = \frac{(\mathrm{CeFOH^+})(\mathrm{H^+})}{(\mathrm{CeF^{2+}})}.$$

Determination of $\Delta(\mathrm{H_{II}}^+)$ required for observed pH change between point A and point B:

$\Delta(\mathrm{H_{II}}^+) = (\mathrm{H^+})$ at pH 4·3, point B $-$ $(\mathrm{H^+})$ at pH 5·8, point A

$= -$ anti log 4·3 $-$ ($-$ anti log 5·8)

$= 5{\cdot}0 \times 10^{-5} - 1{\cdot}8 \times 10^{-6}$

$= 4{\cdot}8 \times 10^{-5}$ mole per l.

$= 1{\cdot}7 \times 10^{-6}$ mole per 35·00 ml of total solution.

Determination of $\mathrm{CeFOH^+}$ from reaction $\mathrm{CeF^{2+} + H_2O = CeFOH^+ + H^+}$:

(HF) and $(\mathrm{CeOH^{2+}})$ dissociate forming $\mathrm{H^+}$ and $\mathrm{OH^-}$ respectively when $\mathrm{Ce^{3+}}$ combines with $\mathrm{F^-}$ to form $\mathrm{CeF^{2+}}$.

$(\mathrm{CeFOH^+}) = (\mathrm{H^+})$ from hydrolysis of $\mathrm{CeF^{2+}}$

$= \Delta(\mathrm{H_{II}}^+)$ required/35·00 ml sol. $-$ $(\mathrm{H^+})$ from HF/3·33 ml sol. $+$ $(\mathrm{OH^-})$ from $\mathrm{CeOH^{2+}}$/35·00 ml sol.

$= \Delta(\mathrm{H_{II}}^+) - (\mathrm{HF}) + (\mathrm{CeOH^{2+}})$

$= 1{\cdot}7 \times 10^{-6} - 5{\cdot}0 \times 10^{-7} + 5{\cdot}8 \times 10^{-8}$

$= 1{\cdot}3 \times 10^{-6}$ mole per 35·00 ml solution

$= 3{\cdot}7 \times 10^{-5}$ mole per l.

Determination of $(\mathrm{H^+})$ at pH 4·3, point B:

$(\mathrm{H^+}) = -$ anti log 4·3

$= 5{\cdot}0 \times 10^{-5}$.

Determination of $(\mathrm{CeF^{2+}})$:

$(\mathrm{CeF^{2+}})$ = The original concentration of $\mathrm{Ce^{3+}}$ since the experimental data indicates that the fluoride is added stepwise—the concentration of the complex, $\mathrm{CeFOH^+}$

$= 5{\cdot}7 \times 10^{-3} - 3{\cdot}7 \times 10^{-5} = 5{\cdot}7 \times 10^{-3}$.

Calculation of K_h for $\mathrm{CeF^{2+}}$:

$$K_h = \frac{(\mathrm{CeFOH^+})(\mathrm{H^+})}{(\mathrm{CeF^{2+}})} = \frac{3{\cdot}7 \times 10^{-5}(5{\cdot}0 \times 10^{-5})}{5{\cdot}7 \times 10^{-3}}$$

$= 3{\cdot}2 \times 10^{-7}$.

IV. *Calculation of hydrolysis constant for* $\mathrm{CeF_2^+}$, *assuming the reaction* $\mathrm{CeF_2^+ + H_2O = CeF_2OH + H^+}$, *point B to point C.*

$$K_h = \frac{(\mathrm{CeF_2OH})(\mathrm{H^+})}{(\mathrm{CeF_2^+})}.$$

Determination of $\Delta(H^+_{III})$ required for observed pH change from point B to point C:

$$
\begin{aligned}
\Delta(H^+_{III}) &= (H^+) \text{ at pH } 4{\cdot}2 - (H^+) \text{ at pH } 4{\cdot}3 \\
&= -\text{anti log } 4{\cdot}2 - (-\text{anti log } 4{\cdot}3) \\
&= 6{\cdot}3 \times 10^{-5} - 5{\cdot}0 \times 10^{-5} \\
&= 1{\cdot}3 \times 10^{-5} \text{ mole per l.} \\
&= 4{\cdot}6 \times 10^{-7} \text{ mole per } 35{\cdot}00 \text{ ml of solution.}
\end{aligned}
$$

Determination of (OH^-) from the reaction $CeFOH^+ + F^- = CeF_2^+ + OH^-$:

$$
\begin{aligned}
(OH^-) &= (CeFOH^+) \text{ determined in part III} \\
&= 1{\cdot}3 \times 10^{-6} \text{ mole per } 35{\cdot}00 \text{ ml of solution.}
\end{aligned}
$$

Determination of (CeF_2OH) in the reaction $CeF_2^+ + H_2O = CeF_2OH + H^+$:

$$
\begin{aligned}
(CeF_2OH)/35{\cdot}00 \text{ ml sol} &= (H^+) \text{ from hydrolysis of } CeF_2^+ \\
&= \Delta(H^+_{III}) \text{ required}/35 \text{ ml} - (H^+) \text{ from HF}/3{\cdot}3 \text{ ml} + (OH^-) \text{ from } CeFOH^+/35 \text{ ml} \\
&= 4{\cdot}6 \times 10^{-7} - 5{\cdot}0 \times 10^{-7} + 1{\cdot}3 \times 10^{-6} \\
&= 1{\cdot}3 \times 10^{-6} \text{ mole per } 35{\cdot}00 \text{ ml solution} \\
&= 3{\cdot}7 \times 10^{-5} \text{ mole per l.}
\end{aligned}
$$

Determination of (CeF_2^+):

(CeF_2^+) = original concentration of Ce^{3+} since data indicates that the fluorides are added stepwise-the concentration of the complex

$$
\begin{aligned}
&= \text{original } (Ce^{3+}) - (CeF_2OH) \\
&= 5{\cdot}7 \times 10^{-3} - 3{\cdot}7 \times 10^{-5} = 5{\cdot}7 \times 10^{-3}.
\end{aligned}
$$

Calculation of K_h for CeF_2^+:

$$
\begin{aligned}
K_h &= \frac{(CeF_2OH)(H^+) \text{ at pH } 4{\cdot}2, \text{ point C}}{\text{original } (Ce^{3+}) - (CeF_2OH)} \\
&= \frac{3{\cdot}7 \times 10^{-5}(6{\cdot}3 \times 10^{-5})}{5{\cdot}7 \times 10^{-3} - 3{\cdot}7 \times 10^{-5}} \\
&= 4{\cdot}1 \times 10^{-7}.
\end{aligned}
$$