

Chemistry

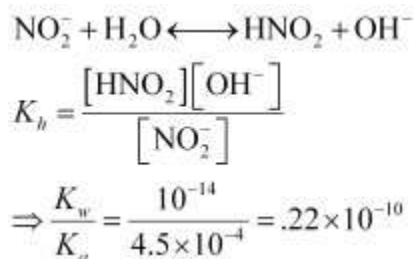
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(Chapter – 7) (Equilibrium)
(Class – XI)

Question 7.61:

The ionization constant of nitrous acid is 4.5×10^{-4} . Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

Answer 7.61:

NaNO_2 is the salt of a strong base (NaOH) and a weak acid (HNO_2).



Now, If x moles of the salt undergo hydrolysis, then the concentration of various species present in the solution will be:

$$[\text{NO}_2^-] = .04 - x ; 0.04$$
$$[\text{HNO}_2] = x$$
$$[\text{OH}^-] = x$$
$$K_h = \frac{x^2}{0.04} = 0.22 \times 10^{-10}$$
$$x^2 = .0088 \times 10^{-10}$$
$$x = .093 \times 10^{-5}$$
$$\therefore [\text{OH}^-] = 0.093 \times 10^{-5} \text{ M}$$
$$[\text{H}_3\text{O}^+] = \frac{10^{-14}}{.093 \times 10^{-5}} = 10.75 \times 10^{-9} \text{ M}$$
$$\Rightarrow \text{pH} = -\log(10.75 \times 10^{-9})$$
$$= 7.96$$

Therefore, degree of hydrolysis

$$= \frac{x}{0.04} = \frac{.093 \times 10^{-5}}{.04}$$
$$= 2.325 \times 10^{-5}$$



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Question 7.62:

A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine

Answer 7.62:

$$\text{pH} = 3.44$$

We know that,

$$\text{pH} = -\log [\text{H}^+]$$

$$\therefore [\text{H}^+] = 3.63 \times 10^{-4}$$

$$\text{Then, } K_b = \frac{(3.63 \times 10^{-4})^2}{0.02} \quad (\because \text{concentration} = 0.02 \text{ M})$$

$$\Rightarrow K_b = 6.6 \times 10^{-6}$$

$$\text{Now, } K_b = \frac{K_w}{K_a}$$

$$\begin{aligned} \Rightarrow K_a &= \frac{K_w}{K_b} = \frac{10^{-14}}{6.6 \times 10^{-6}} \\ &= 1.51 \times 10^{-9} \end{aligned}$$

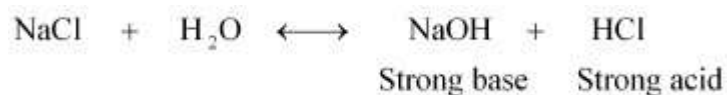
Question 7.63:

Predict if the solutions of the following salts are neutral, acidic or basic:

NaCl, KBr, NaCN, NH_4NO_3 , NaNO_2 and KF

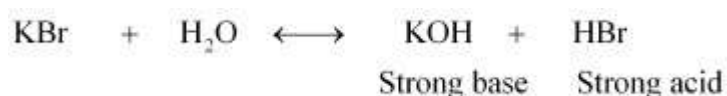
Answer 7.63:

(i) NaCl:



Therefore, it is a neutral solution.

(ii) KBr:

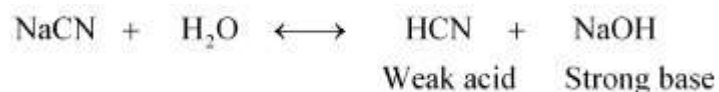


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Therefore, it is a neutral solution.

(iii) NaCN:



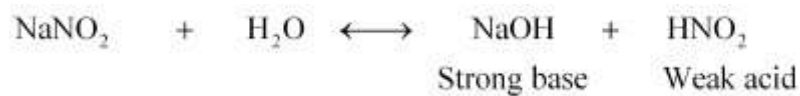
Therefore, it is a basic solution.

(iv) NH₄NO₃



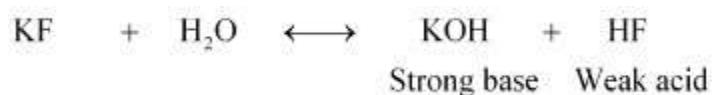
Therefore, it is an acidic solution.

(v) NaNO₂



Therefore, it is a basic solution.

(vi) KF



Therefore, it is a basic solution.

Question 7.64:

The ionization constant of chloroacetic acid is 1.35×10^{-3} . What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

Answer 7.64:

It is given that K_a for ClCH₂COOH is 1.35×10^{-3} .



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$$\Rightarrow K_a = c\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.35 \times 10^{-3}}{0.1}}$$

(\therefore concentration of acid = 0.1m)

$$\alpha = \sqrt{1.35 \times 10^{-2}}$$
$$= 0.116$$

$$\therefore [\text{H}^+] = c\alpha = 0.1 \times 0.116$$
$$= .0116$$

$$\Rightarrow \text{pH} = -\log[\text{H}^+] = 1.94$$

$\text{ClCH}_2\text{COONa}$ is the salt of a weak acid i.e., ClCH_2COOH and a strong base i.e., NaOH .



$$K_b = \frac{[\text{ClCH}_2\text{COOH}][\text{OH}^-]}{[\text{ClCH}_2\text{COO}^-]}$$

$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{10^{-14}}{1.35 \times 10^{-3}}$$

$$= 0.740 \times 10^{-11}$$

$$\text{Also, } K_b = \frac{x^2}{0.1}$$

(where x is the concentration of OH^- and ClCH_2COOH)

$$0.740 \times 10^{-11} = \frac{x^2}{0.1}$$

$$0.074 \times 10^{-11} = x^2$$

$$\Rightarrow x^2 = 0.74 \times 10^{-12}$$

$$x = 0.86 \times 10^{-6}$$

$$[\text{OH}^-] = 0.86 \times 10^{-6}$$

$$\therefore [\text{H}^+] = \frac{K_w}{0.86 \times 10^{-6}}$$

$$= \frac{10^{-14}}{0.86 \times 10^{-6}}$$

$$[\text{H}^+] = 1.162 \times 10^{-8}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$= 7.94$$

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Question 7.65:

Ionic product of water at 310 K is 2.7×10^{-14} . What is the pH of neutral water at this temperature?

Answer 7.65:

Ionic product,

$$\begin{aligned}K_w &= [\text{H}^+][\text{OH}^-] \\ \text{Let } [\text{H}^+] &= x. \\ \text{Since } [\text{H}^+] &= [\text{OH}^-], K_w = x^2. \\ \Rightarrow K_w \text{ at } 310\text{K} & \text{ is } 2.7 \times 10^{-14}. \\ \therefore 2.7 \times 10^{-14} &= x^2 \\ \Rightarrow x &= 1.64 \times 10^{-7} \\ \Rightarrow [\text{H}^+] &= 1.64 \times 10^{-7} \\ \Rightarrow \text{pH} &= -\log [\text{H}^+] \\ &= -\log [1.64 \times 10^{-7}] \\ &= 6.78\end{aligned}$$

Hence, the pH of neutral water is 6.78.

Question 7.66:

Calculate the pH of the resultant mixtures:

- a) 10 mL of 0.2M $\text{Ca}(\text{OH})_2$ + 25 mL of 0.1M HCl
- b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $\text{Ca}(\text{OH})_2$
- c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

Answer 7.66:

(a) Moles of H_3O^+ = $\frac{25 \times 0.1}{1000} = .0025 \text{ mol}$

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$$\text{Moles of OH}^- = \frac{10 \times 0.2 \times 2}{1000} = .0040 \text{ mol}$$

Thus, excess of $\text{OH}^- = .0015 \text{ mol}$

$$[\text{OH}^-] = \frac{.0015}{35 \times 10^{-3}} \text{ mol/L} = .0428$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= 1.36$$

$$\text{pH} = 14 - 1.36$$

$$= 12.63 \quad (\text{not matched})$$

(b) Moles of $\text{H}_3\text{O}^+ = \frac{2 \times 10 \times 0.01}{1000} = .0002 \text{ mol}$

$$\text{Moles of OH}^- = \frac{2 \times 10 \times .01}{1000} = .0002 \text{ mol}$$

Since there is neither an excess of H_3O^+ or OH^-

(c) Moles of $\text{H}_3\text{O}^+ = \frac{2 \times 10 \times 0.1}{1000} = .002 \text{ mol}$

$$\text{Moles of OH}^- = \frac{10 \times 0.1}{1000} = 0.001 \text{ mol}$$

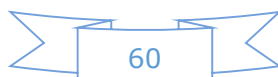
Excess of $\text{H}_3\text{O}^+ = .001 \text{ mol}$

$$\text{Thus, } [\text{H}_3\text{O}^+] = \frac{.001}{20 \times 10^{-3}} = \frac{10^{-3}}{20 \times 10^{-3}} = .05$$

$$\therefore \text{pH} = -\log(0.05)$$

$$= 1.30$$

The solution is neutral. Hence, $\text{pH} = 7$.



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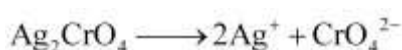
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Question 7.67:

Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9 (page 221). Determine also the molarities of individual ions.

Answer 7.67:

(1) Silver chromate:



Then,

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

Let the solubility of Ag_2CrO_4 be s .

$$\Rightarrow [\text{Ag}^+] = 2s \text{ and } [\text{CrO}_4^{2-}] = s$$

Then,

$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

$$\Rightarrow 1.1 \times 10^{-12} = 4s^3$$

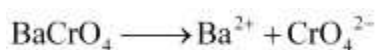
$$.275 \times 10^{-12} = s^3$$

$$s = 0.65 \times 10^{-4} \text{ M}$$

$$\text{Molarity of } \text{Ag}^+ = 2s = 2 \times 0.65 \times 10^{-4} = 1.30 \times 10^{-4} \text{ M}$$

$$\text{Molarity of } \text{CrO}_4^{2-} = s = 0.65 \times 10^{-4} \text{ M}$$

(2) Barium chromate:



$$\text{Then, } K_{sp} = [\text{Ba}^{2+}] [\text{CrO}_4^{2-}]$$

Let the solubility of BaCrO_4 be s .

$$\begin{aligned} \text{So, } [\text{Ba}^{2+}] = s \text{ and } [\text{CrO}_4^{2-}] = s &\Rightarrow K_{sp} = s^2 \\ &\Rightarrow 1.2 \times 10^{-10} = s^2 \\ &\Rightarrow s = 1.09 \times 10^{-5} \text{ M} \end{aligned}$$

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Molarity of Ba^{2+} = Molarity of $\text{CrO}_4^{2-} = s = 1.09 \times 10^{-5} \text{ M}$

(3) Ferric hydroxide:



$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3$$

Let s be the solubility of $\text{Fe}(\text{OH})_3$.

$$\text{Thus, } [\text{Fe}^{3+}] = s \text{ and } [\text{OH}^-] = 3s \Rightarrow K_{sp} = s.(3s)^3 \\ = s.27s^3$$

$$K_{sp} = 27s^4$$

$$1.0 \times 10^{-38} = 27s^4$$

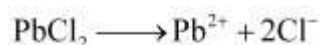
$$.037 \times 10^{-38} = s^4$$

$$.00037 \times 10^{-36} = s^4 \Rightarrow 1.39 \times 10^{-10} \text{ M} = S$$

Molarity of $\text{Fe}^{3+} = s = 1.39 \times 10^{-10} \text{ M}$

Molarity of $\text{OH}^- = 3s = 4.17 \times 10^{-10} \text{ M}$

(4) Lead chloride:



$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

Let K_{sp} be the solubility of PbCl_2 .

$$[\text{Pb}^{2+}] = s \text{ and } [\text{Cl}^-] = 2s$$

$$\text{Thus, } K_{sp} = s.(2s)^2$$

$$= 4s^3$$

$$\Rightarrow 1.6 \times 10^{-5} = 4s^3$$

$$\Rightarrow 0.4 \times 10^{-5} = s^3$$

$$4 \times 10^{-6} = s^3 \Rightarrow 1.58 \times 10^{-2} \text{ M} = S.1$$

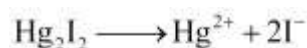
Molarity of $\text{Pb}^{2+} = s = 1.58 \times 10^{-2} \text{ M}$

Molarity of chloride = $2s = 3.16 \times 10^{-2} \text{ M}$

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(5) Mercurous iodide:



$$K_{sp} = [\text{Hg}_2^{2+}]^2 [\text{I}^-]^2$$

Let s be the solubility of Hg_2I_2 .

$$\Rightarrow [\text{Hg}_2^{2+}] = s \text{ and } [\text{I}^-] = 2s$$

$$\text{Thus, } K_{sp} = s(2s)^2 \Rightarrow K_{sp} = 4s^3$$

$$4.5 \times 10^{-29} = 4s^3$$

$$1.125 \times 10^{-29} = s^3$$

$$\Rightarrow s = 2.24 \times 10^{-10} \text{ M}$$

Molarity of $\text{Hg}_2^{2+} = s = 2.24 \times 10^{-10} \text{ M}$

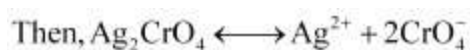
Molarity of $\text{I}^- = 2s = 4.48 \times 10^{-10} \text{ M}$

Question 7.68:

The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Answer 7.68:

Let s be the solubility of Ag_2CrO_4 .



$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

$$1.1 \times 10^{-12} = 4s^3$$

$$s = 6.5 \times 10^{-5} \text{ M}$$

Let s' be the solubility of AgBr .



$$K_{sp} = s'^2 = 5.0 \times 10^{-13}$$

$$\therefore s' = 7.07 \times 10^{-7} \text{ M}$$

Therefore, the ratio of the molarities of their saturated solution is

$$\frac{s}{s'} = \frac{6.5 \times 10^{-5} \text{ M}}{7.07 \times 10^{-7} \text{ M}} = 91.9.$$

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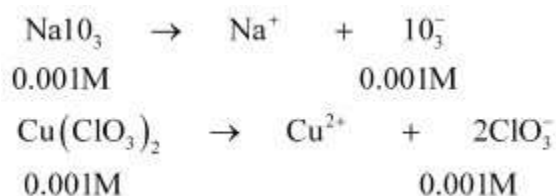
Question 7.69:

Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate?

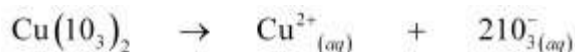
(For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

Answer 7.69:

When equal volumes of sodium iodate and cupric chlorate solutions are mixed together, then the molar concentrations of both solutions are reduced to half i.e., 0.001 M. Then,



Now, the solubility equilibrium for copper iodate can be written as:



Ionic product of copper iodate:

$$\begin{aligned} &= [\text{Cu}^{2+}][\text{IO}_3^-]^2 \\ &= (0.001)(0.001)^2 \\ &= 1 \times 10^{-9} \end{aligned}$$

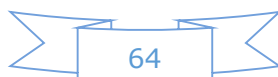
Since the ionic product (1×10^{-9}) is less than K_{sp} (7.4×10^{-8}), precipitation will not occur.

Question 7.70:

The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13} . How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

Answer 7.70:

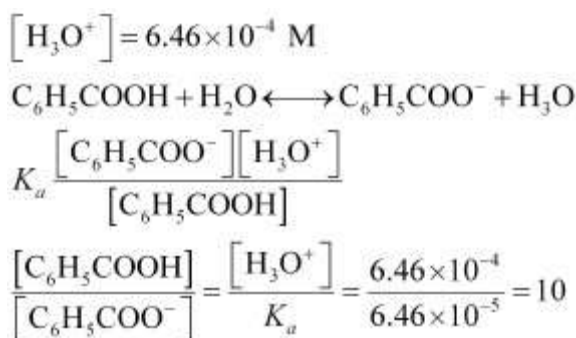
Since pH = 3.19,



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Let the solubility of $\text{C}_6\text{H}_5\text{COOAg}$ be x mol/L.

Then,

$$\begin{aligned}[\text{Ag}^+] &= x \\ [\text{C}_6\text{H}_5\text{COOH}] + [\text{C}_6\text{H}_5\text{COO}^-] &= x \\ 10[\text{C}_6\text{H}_5\text{COO}^-] + [\text{C}_6\text{H}_5\text{COO}^-] &= x \\ [\text{C}_6\text{H}_5\text{COO}^-] &= \frac{x}{11} \\ K_{sp} [\text{Ag}^+] [\text{C}_6\text{H}_5\text{COO}^-] & \\ 2.5 \times 10^{-13} &= x \left(\frac{x}{11} \right) \\ x &= 1.66 \times 10^{-6} \text{ mol/L}\end{aligned}$$

Thus, the solubility of silver benzoate in a pH 3.19 solution is 1.66×10^{-6} mol/L.

Now, let the solubility of $\text{C}_6\text{H}_5\text{COOAg}$ be x' mol/L.

$$\begin{aligned}\text{Then, } [\text{Ag}^+] &= x' \text{ M and } [\text{CH}_3\text{COO}^-] = x' \text{ M.} \\ K_{sp} &= [\text{Ag}^+] [\text{CH}_3\text{COO}^-] \\ K_{sp} &= (x')^2 \\ x' &= \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ mol/L} \\ \therefore \frac{x}{x'} &= \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32\end{aligned}$$

Hence, $\text{C}_6\text{H}_5\text{COOAg}$ is approximately 3.317 times more soluble in a low pH solution.



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Question 7.71:

What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).

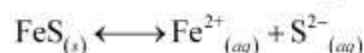
Answer 7.71:

Let the maximum concentration of each solution be x mol/L. After mixing, the volume of the concentrations of each solution will be reduced to half i.e., $x/2$.

$$\therefore [\text{FeSO}_4] = [\text{Na}_2\text{S}] = \frac{x}{2} \text{ M}$$

$$\text{Then, } [\text{Fe}^{2+}] = [\text{FeSO}_4] = \frac{x}{2} \text{ M}$$

$$\text{Also, } [\text{S}^{2-}] = [\text{Na}_2\text{S}] = \frac{x}{2} \text{ M}$$



$$K_{sp} = [\text{Fe}^{2+}][\text{S}^{2-}]$$

$$6.3 \times 10^{-18} = \left(\frac{x}{2}\right)\left(\frac{x}{2}\right)$$

$$\frac{x^2}{4} = 6.3 \times 10^{-18}$$

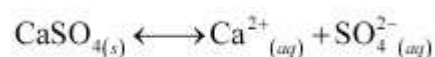
$$\Rightarrow x = 5.02 \times 10^{-9}$$

If the concentrations of both solutions are equal to or less than 5.02×10^{-9} M, then there will be no precipitation of iron sulphide.

Question 7.72:

What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

Answer 7.72:



$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

Let the solubility of CaSO_4 be s .

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$$\text{Then, } K_{sp} = s^2$$

$$9.1 \times 10^{-6} = s^2$$

$$s = 3.02 \times 10^{-3} \text{ mol/L}$$

Molecular mass of $\text{CaSO}_4 = 136 \text{ g/mol}$

Solubility of CaSO_4 in gram/L

$$= 3.02 \times 10^{-3} \times 136$$

$$= 0.41 \text{ g/L}$$

This means that we need 1L of water to dissolve 0.41g of CaSO_4

Therefore, to dissolve 1g of CaSO_4 we require $= \frac{1}{0.41} \text{ L} = 2.44 \text{ L}$ of water.

Question 7.73:

The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is $1.0 \times 10^{-19} \text{ M}$. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: FeSO_4 , MnCl_2 , ZnCl_2 and CdCl_2 . in which of these solutions precipitation will take place?

$$\text{Given } K_{sp} \text{ for } \text{FeS} = 6.3 \times 10^{-18}, \text{ MnS} = 2.5 \times 10^{-13}, \text{ ZnS} = 1.6 \times 10^{-24}, \\ \text{CdS} = 8.0 \times 10^{-27}$$

Answer 7.73:

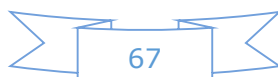
For precipitation to take place, it is required that the calculated ionic product exceeds the K_{sp} value.

Before mixing:

$$[\text{S}^{2-}] = 1.0 \times 10^{-19} \text{ M} \quad [\text{M}^{2+}] = 0.04 \text{ M}$$

$$\text{volume} = 10 \text{ mL} \quad \text{volume} = 5 \text{ mL}$$

After mixing:



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$$[S^{2-}] = ?$$

$$\text{volume} = (10 + 5) = 15 \text{ mL}$$

$$[M^{2+}] = ?$$

$$\text{volume} = 15 \text{ mL}$$

$$[S^{2-}] = \frac{1.0 \times 10^{-19} \times 10}{15} = 6.67 \times 10^{-20} \text{ M}$$

$$[M^{2+}] = \frac{0.04 \times 5}{15} = 1.33 \times 10^{-2} \text{ M}$$

$$\begin{aligned} \text{Ionic product} &= [M^{2+}][S^{2-}] \\ &= (1.33 \times 10^{-2})(6.67 \times 10^{-20}) \\ &= 8.87 \times 10^{-22} \end{aligned}$$

This ionic product exceeds the K_{sp} of ZnS and CdS. Therefore, precipitation will occur in CdCl₂ and ZnCl₂ solutions.