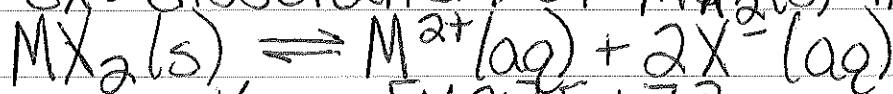


# Precipitation Equilibria

- Solubility Product Constant ( $K_{sp}$ ) - equilibrium constant indicating how soluble the solid is in water

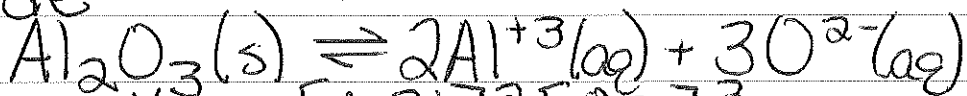
ex: dissolution of  $MX_2(s)$  in solution



$$K_{sp} = [M^{2+}][X^{-}]^2$$

\*  $K$  is constant for a given temp, independent of ion concentrations, constant for equation as written

- ex. Write the  $K_{sp}$  expression for aluminum oxide



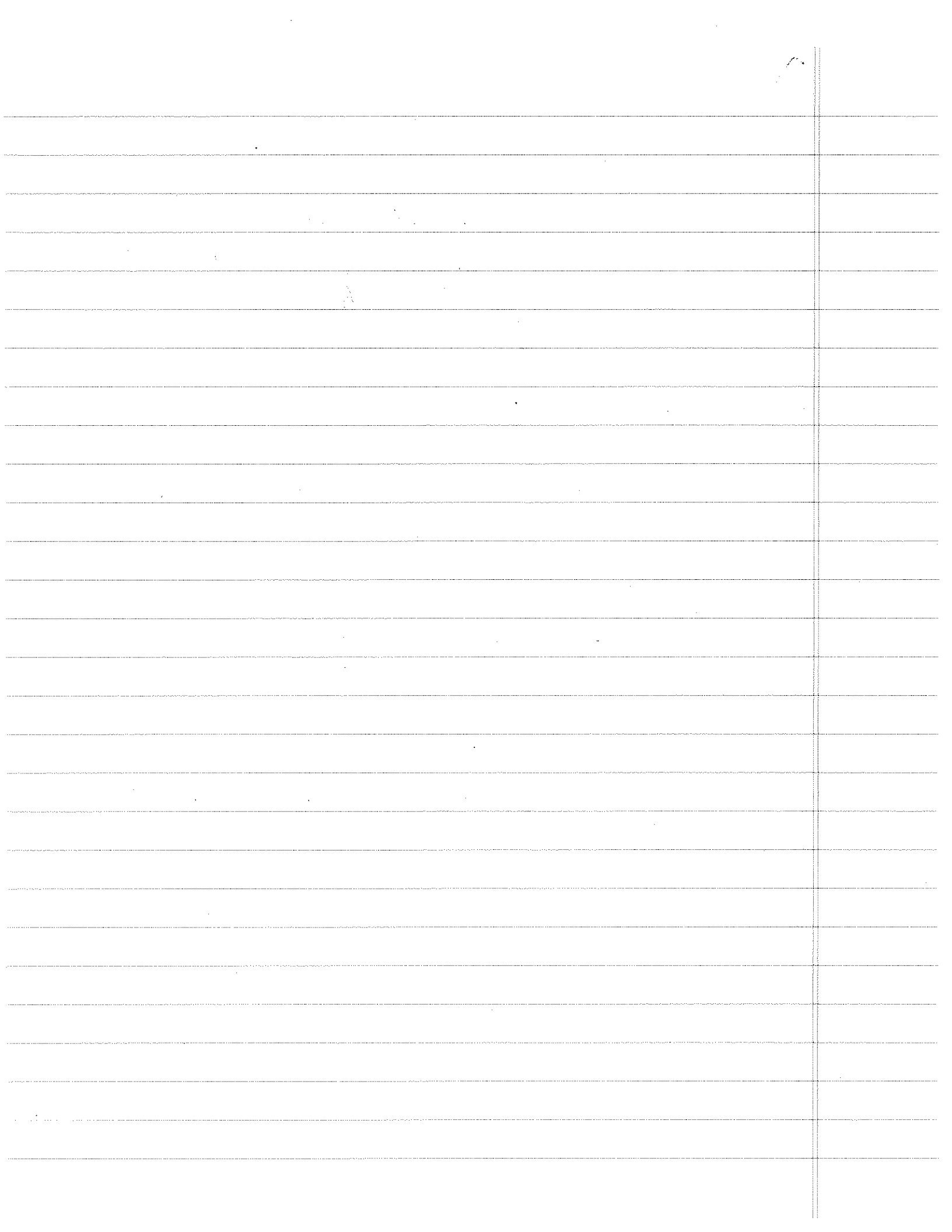
$$K_{sp} = [Al^{3+}]^2 [O^{2-}]^3$$

- ex. Write the  $K_{sp}$  expression for nickel (II) chloride

$$K_{sp} = [Ni^{2+}][Cl^{-}]^2$$

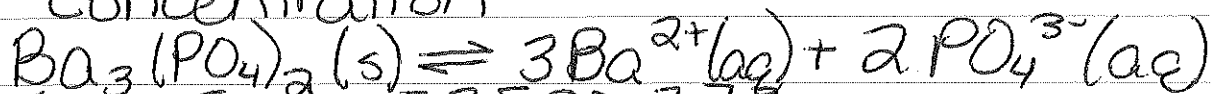
- ex. Write the  $K_{sp}$  expression for potassium permanganate

$$K_{sp} = [K^{+}][MnO_4^{-}]$$



Using  $K_{sp}$ :

- ex. A solution in equilibrium with barium phosphate solid has a barium ion concentration of  $5 \times 10^{-4} M$ .  $K_{sp}$  of  $Ba_3(PO_4)_2$  is  $6 \times 10^{-39}$ . Calculate phosphate ion concentration

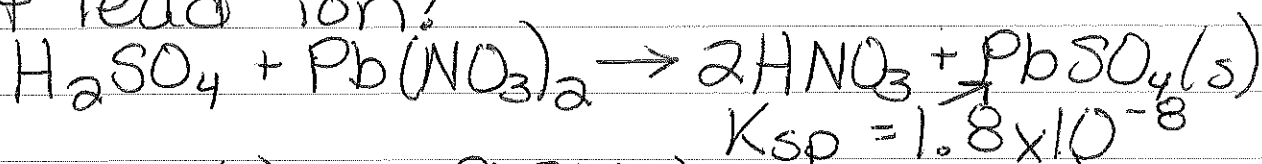


$$K_{sp} = [Ba^{2+}]^3 [PO_4^{3-}]^2$$

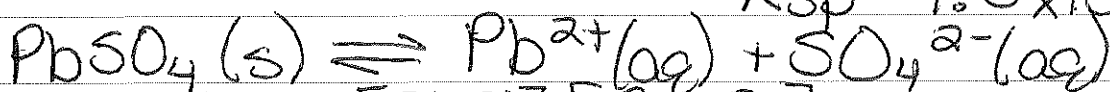
$$6 \times 10^{-39} = (5 \times 10^{-4})^3 [PO_4^{3-}]^2$$

$$[PO_4^{3-}] = 7 \times 10^{-15} M$$

- Sulfuric acid is added to a lead nitrate solution. When equilibrium is established  $[SO_4^{2-}] = 2.0 \times 10^{-4}$ . What is the equilibrium concentration of lead ion?



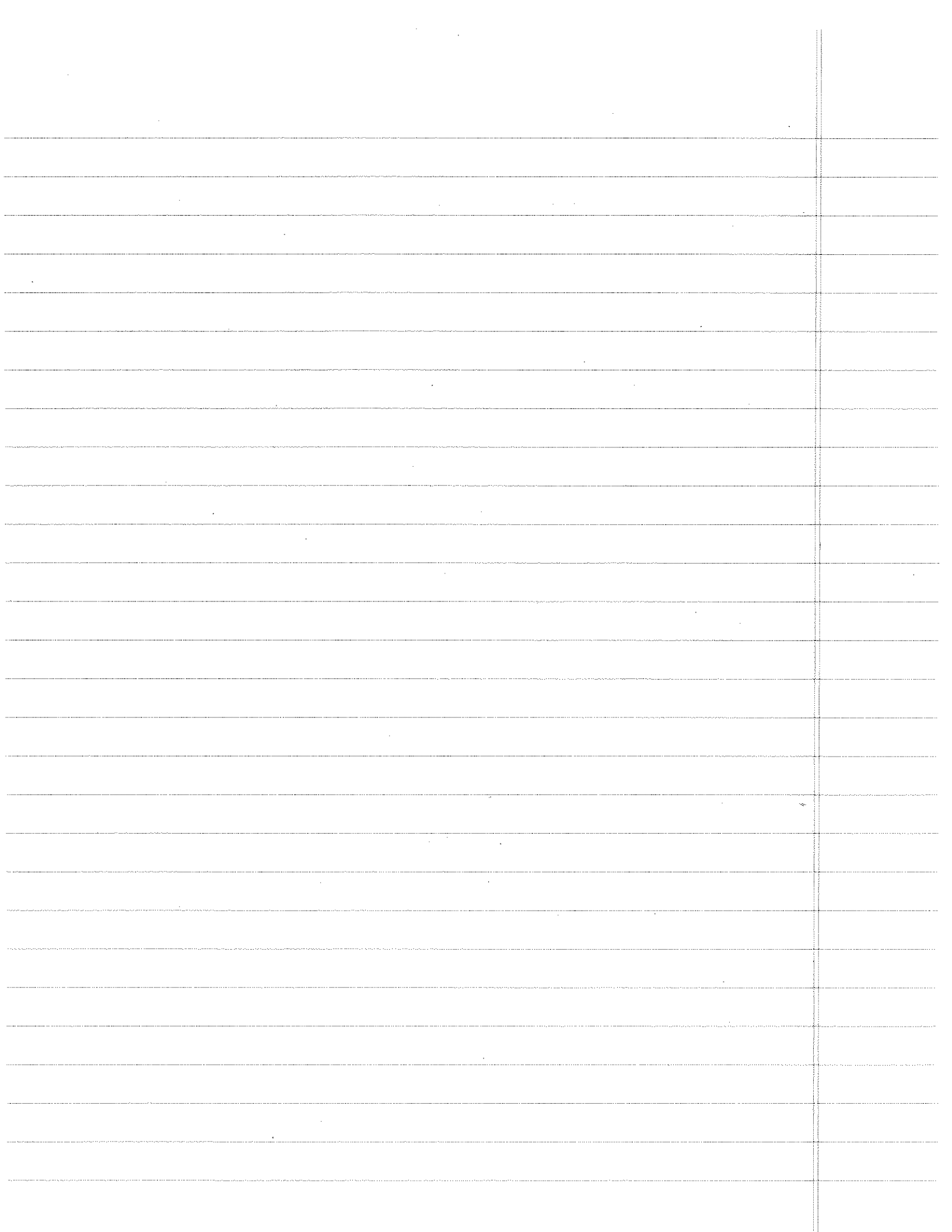
$$K_{sp} = 1.8 \times 10^{-8}$$



$$K_{sp} = [Pb^{2+}] [SO_4^{2-}]$$

$$1.8 \times 10^{-8} = [Pb^{2+}] [2.0 \times 10^{-4}]$$

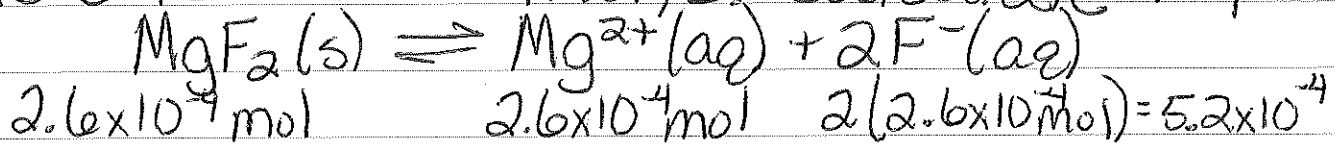
$$[Pb^{2+}] = 9.0 \times 10^{-5}$$



## K<sub>sp</sub> and Solubility

- Solubility expressed in mol/L or M.

ex. The measured solubility of MgF<sub>2</sub> at 25°C is  $2.6 \times 10^{-4}$  mol/L. Calculate K<sub>sp</sub>



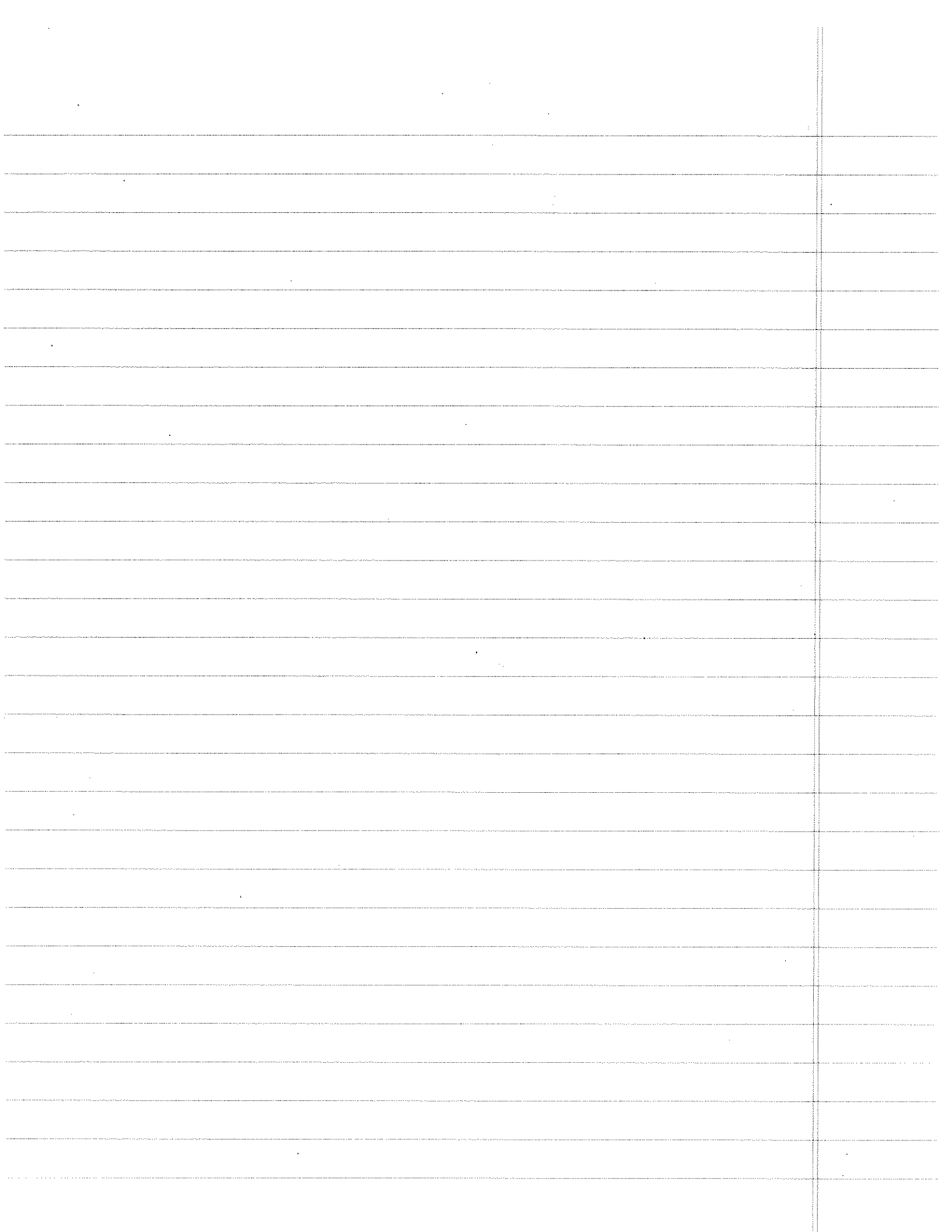
$$\begin{aligned} K_{sp} &= [\text{Mg}^{2+}][\text{F}^{-}]^2 \\ &= (2.6 \times 10^{-4})(5.2 \times 10^{-4})^2 = 7.0 \times 10^{-11} \end{aligned}$$

ex. BaC<sub>2</sub>O<sub>4</sub> has a solubility of 22 mg/L. What is the K<sub>sp</sub> for BaC<sub>2</sub>O<sub>4</sub>?



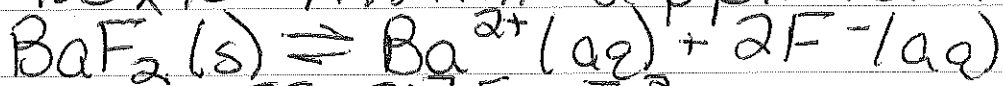
$$22 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol}}{225 \text{ g}} = \frac{9.78 \times 10^{-5} \text{ mol}}{\text{L}} \text{ BaC}_2\text{O}_4$$

$$K_{sp} = (9.78 \times 10^{-5})^2 = 9.56 \times 10^{-9}$$



Using  $K_{sp}$  to know whether ppt. forms:  
 ex. A solution of  $0.020M$  fluoride ions is added to a solution in which the original concentration of barium ions is  $1.0 \times 10^{-4}M$ . Will a ppt. form?

$K_{sp}$  of  $BaF_2 = 1.8 \times 10^{-7}$



$$Q = [Ba^{2+}][F^{-}]^2$$

$$Q = (1.0 \times 10^{-4})(2.0 \times 10^{-2})^2$$

$$Q = 4.0 \times 10^{-8}$$

$Q < K_{sp}$  and a ppt. will not form.

see above

ex. What concentration of  $F^{-}$  is needed to get a saturated soln?

At saturation  $Q = K_{sp}$ .

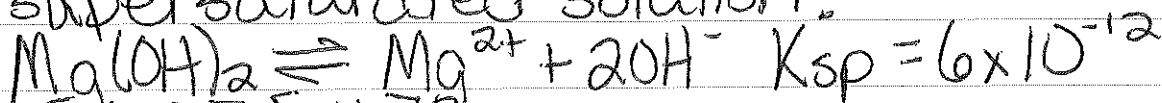
$$K_{sp} = [Ba^{2+}][F^{-}]^2$$

$$1.8 \times 10^{-7} = (1.0 \times 10^{-4})[F^{-}]^2$$

$$[F^{-}] = 4.2 \times 10^{-2}M$$

$\therefore$  When  $[F^{-}]$  is greater than  $4.2 \times 10^{-2}M$ , there will be a ppt. ( $Q > K_{sp}$ )

ex. A soln. originally contains  $0.003M$   $Mg^{2+}$ . What concentration of  $OH^{-}$  ions should be added to give an unsaturated, saturated, and supersaturated solution?



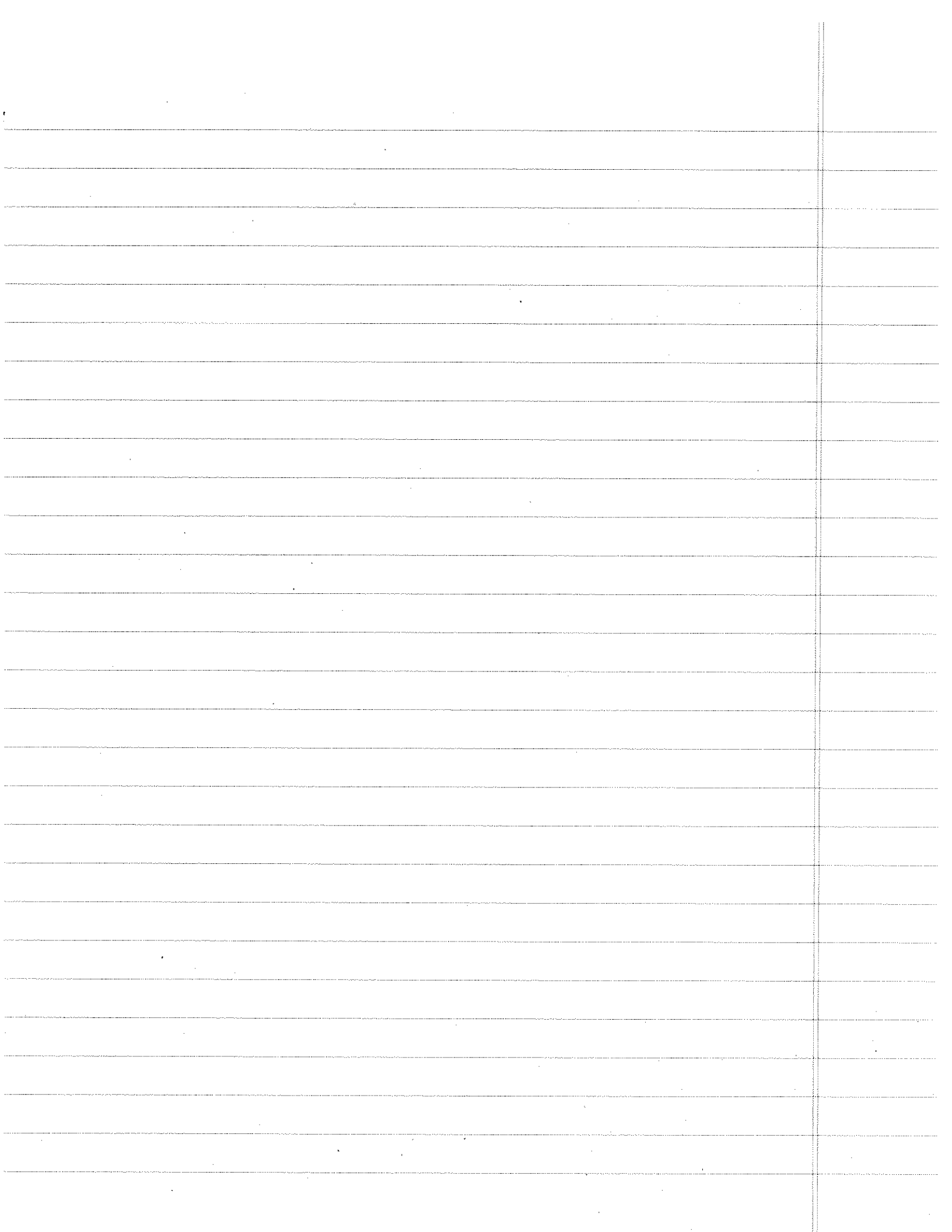
$$K_{sp} = [Mg^{2+}][OH^{-}]^2$$

$$6 \times 10^{-12} = [0.003][OH^{-}]^2$$

$$[OH^{-}] = 4.4 \times 10^{-5}$$

saturated

$> 4.4 \times 10^{-5}$  supersaturated  
 $< 4.4 \times 10^{-5}$  unsaturated





## Using $K_{sp}$ : Mixing Solutions

ex. Will a ppt. form when 200.0 mL of 0.100 M  $\text{Al}(\text{NO}_3)_3$  is mixed with 300.0 mL  $\text{Ba}(\text{OH})_2$ ?

Determine the ppt. using solubility rules:  
 $\text{Al}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3\text{OH}^{-}(\text{aq})$   
 $K_{sp} = 2 \times 10^{-31}$

Is there enough  $\text{Al}^{3+}$  and  $\text{OH}^{-}$  ions in solution for  $Q > K_{sp}$ ?

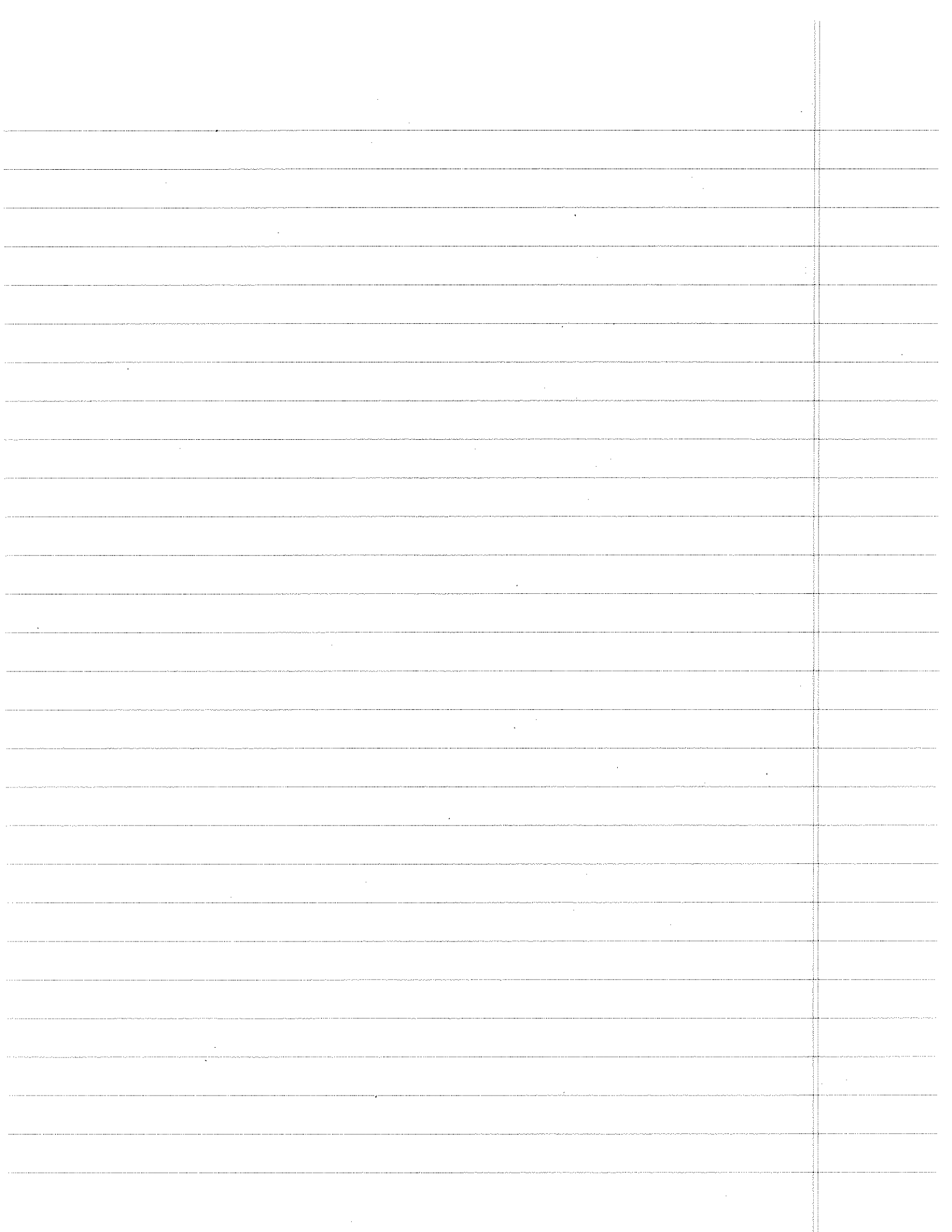
$$\text{For } \text{Al}^{3+}: 0.200\text{L} \times \frac{0.100\text{mol } \text{Al}(\text{NO}_3)_3}{1\text{L}} \times \frac{1\text{mol } \text{Al}^{3+}}{1\text{mol } \text{Al}(\text{NO}_3)_3} = 0.0200\text{mol } \text{Al}^{3+}$$
$$0.0200\text{mol } \text{Al}^{3+} \times \frac{1}{0.200\text{L} + 0.300\text{L}} = 0.0400\text{M } \text{Al}^{3+}$$

$$\text{For } \text{OH}^{-}: 0.300\text{L} \times \frac{0.200\text{mol } \text{Ba}(\text{OH})_2}{1\text{L}} \times \frac{2\text{mol } \text{OH}^{-}}{1\text{mol } \text{Ba}(\text{OH})_2} = 0.120\text{mol } \text{OH}^{-}$$
$$0.120\text{mol } \text{OH}^{-} \times \frac{1}{0.200\text{L} + 0.300\text{L}} = 0.240\text{M } \text{OH}^{-}$$

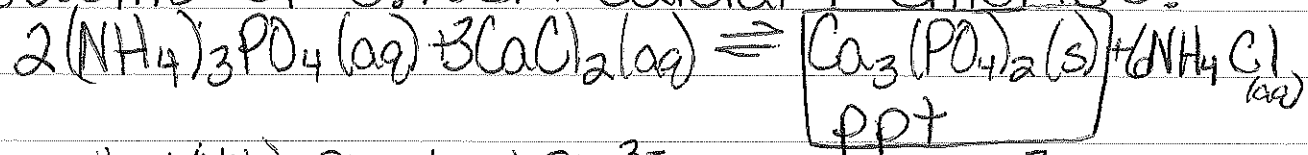
$$Q = [\text{Al}^{3+}][\text{OH}^{-}]^3$$

$$Q = [0.0400][0.240]^3 = 5.53 \times 10^{-4}$$

$Q > K$ ,  $\therefore$  a ppt. will form



ex. Will a ppt. form if 250.0 mL of 0.400 M ammonium phosphate are mixed with 450.0 mL of 0.125 M calcium chloride?

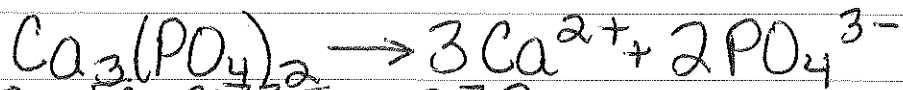


For  $\text{PO}_4^{3-}$

$$0.25\text{L} \times \frac{0.4\text{mol}(\text{NH}_4)_3\text{PO}_4}{1\text{L}} \times \frac{1\text{mol PO}_4^{3-}}{1\text{mol}(\text{NH}_4)_3\text{PO}_4} = \frac{0.1\text{mol PO}_4^{3-}}{0.7\text{L}} = 0.143\text{M} = [\text{PO}_4^{3-}]$$

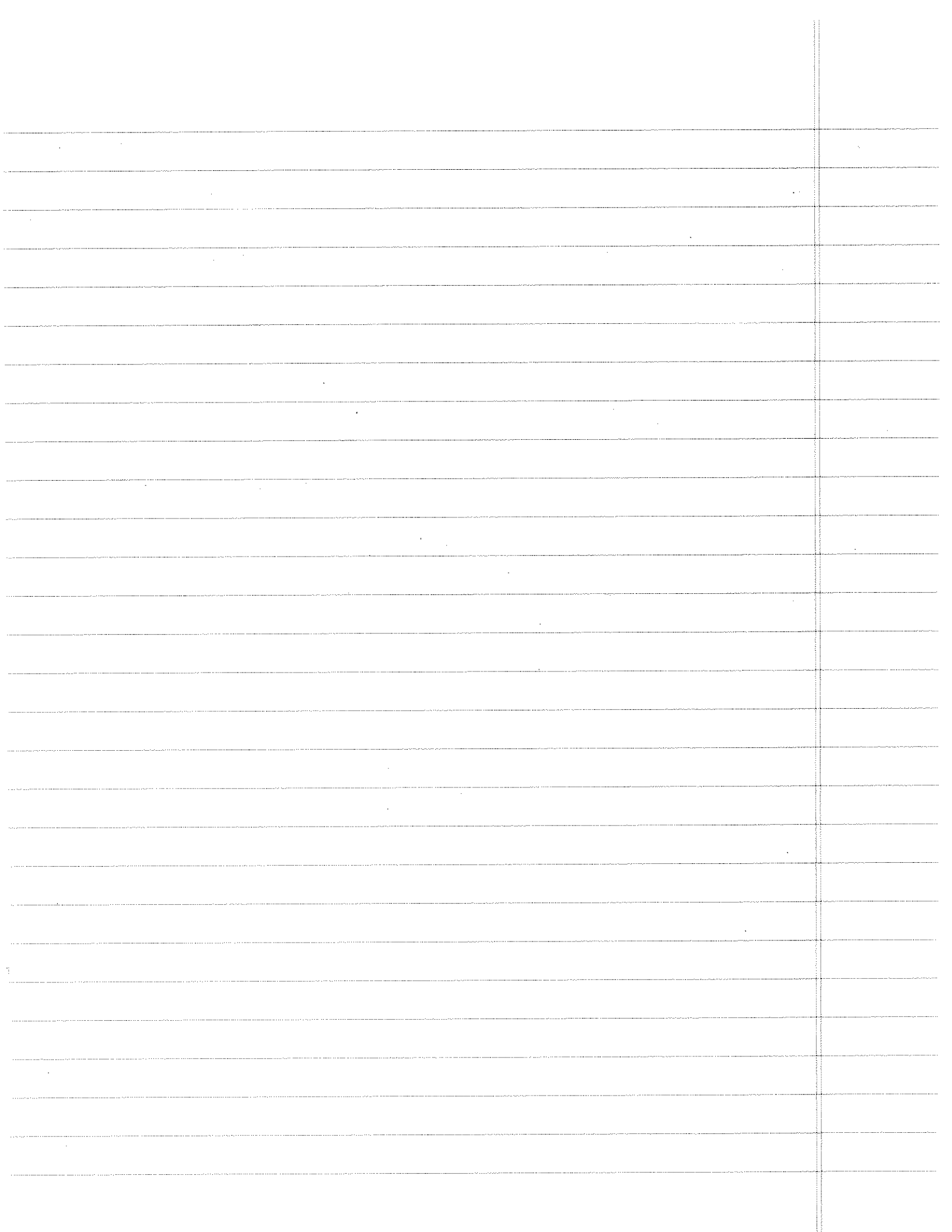
For  $\text{Ca}^{2+}$

$$0.45\text{L} \times \frac{0.125\text{mol CaCl}_2}{1\text{L CaCl}_2} \times \frac{2\text{mol Ca}^{2+}}{1\text{mol CaCl}_2} = \frac{0.05625\text{mol Ca}^{2+}}{0.7\text{L}} = 0.08\text{M} = [\text{Ca}^{2+}]$$



$$Q = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 1.047 \times 10^{-5}$$

$Q > K \therefore$  precipitate forms



Predicting which precipitates forms:

ex.

A soln. contains 0.02M of  $Mg^{2+}$  and 0.02M of  $Sr^{2+}$ . Sufficient carbonate is added so that the carbonate ion concentration is  $2 \times 10^{-7}M$ . Does a ppt. form and if so what is?

For:  $MgCO_3$   $K_{sp} = 6.8 \times 10^{-6}$

$$Q = [Mg^{2+}][CO_3^{2-}]$$
$$= (0.02)(2 \times 10^{-7}) = 4 \times 10^{-9}$$

$Q < K$ ,  $\therefore$  no ppt. forms

For:  $SrCO_3$   $K_{sp} = 5.6 \times 10^{-10}$

$$Q = [Sr^{2+}][CO_3^{2-}]$$
$$= (0.02)(2 \times 10^{-7}) = 4 \times 10^{-9}$$

$Q > K$ ,  $\therefore$   $SrCO_3$  precipitates

ex. A soln. contains 0.0040M  $Ba^{2+}$  and 0.0060M  $Pb^{2+}$ . What concentration of  $F^-$  will precipitate just one of the ions?

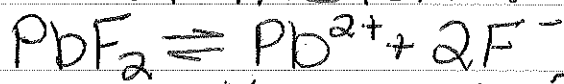


$$K_{sp} = 1.8 \times 10^{-7}$$

$$1.8 \times 10^{-7} = [0.004][F^-]^2$$

$$[F^-] = 6.7 \times 10^{-3}$$

$$.0067M$$



$$K_{sp} = 1.5 \times 10^{-7}$$

$$1.5 \times 10^{-7} = [0.006][F^-]^2$$

$$[F^-] = .005$$

only  $BaF_2$  will ppt.

$\therefore$   $Pb^{2+}$  precipitates selectively when  $[F^-]$  is below  $6.7 \times 10^{-3}M$

