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## QUIZ CH103

Basic Ionic Equilibrium

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PROBLEMS
$\rightarrow$ Problem 1.1
0.32 g of $\mathrm{N}_{2} \mathrm{H}_{4}$ is dissolved in water and the total volume is made up to 500 mL . Calculate the percentage of $\mathrm{N}_{2} \mathrm{H}_{4}$ that has reacted with water if the value of $K_{b}$ for aniline is $3.6 \times 10^{-6} \mathrm{M}$.
A) $\alpha=0.557 \%$
B) $\alpha=1.34 \%$
C) $\alpha=2.68 \%$
D) $\alpha=3.40 \%$

## $\rightarrow$ Problem 1.2

Butyric acid ( $K_{a}=1.6 \times 10^{-5}$ ) dissociates in a water solution. Determine the percent dissociation if the solution in question contains 0.08 mole of butyric acid per liter.
A) $\alpha=0.311 \%$
B) $\alpha=0.577 \%$
C) $\alpha=1.41 \%$
D) $\alpha=2.82 \%$

## $\rightarrow$ Problem 2.1

Pure water, when placed in contact with atmospheric air, absorbs carbon dioxide, $\mathrm{CO}_{2}$, which can be removed by boiling. The dissolution of $\mathrm{CO}_{2}$ in fresh water can be represented by the chemical equation

$$
\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{HCO}_{3}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})
$$

Bromothymol blue is an acid-base indicator that exhibits a yellow color in acid solutions, a green color in neutral solutions, and a blue color in basic solutions. A water sample was boiled and then exposed to air for a long time. Then, bromothymol blue was added to the system. What is the ensuing color of the solution?
$\boldsymbol{\alpha})$ Yellow.
$\boldsymbol{\beta})$ Green.
р) Blue.

## $\rightarrow$ Problem 2.2

The properties of an acid-base indicator are specified in the following chemical equation and figure. True or false?
HInd [aq]

[Yellow] $\longleftrightarrow \quad$| $\mathbf{H}^{+}[a q]+$ Ind $^{-}[\mathrm{aq}]$ |
| :---: |
| [Blue] |


1.( ) When placed in contact with vinegar, the indicator should turn yellow.
2.( ) When placed in contact with ammonia, the indicator should turn green.
3.( ) When placed in contact with sodium acetate, the indicator should turn blue.
4.( ) When placed in contact with sodium chloride, the indicator should turn yellow.

## $\rightarrow$ Problem 2.3

In three different experiments, an aqueous solution of HCl was mixed with an aqueous solution of NaOH . The solutions of both reactants had the same concentration (mol/L). Afterwards, a certain indicator was added, and the following results were obtained.

|  | Reactants | Indicator Color |
| :---: | :---: | :---: |
| Experiment 1 | 2 mL of HCl <br> +1 mL of NaOH | Yellow |
| Experiment 2 | 2 mL of HCl <br> +2 mL of NaOH | Green |
| Experiment 3 | 2 mL of HCl <br> +3 mL of NaOH | Blue |

Consider the following statements.
Statement 1: If this indicator is placed in contact with lemon juice, it will turn yellow.

Statement 2: If the reactants from experiment 1 are mixed with those from experiment 3 , the indicator should turn blue.
A) Both statements are true.
B) Statement 1 is true and statement 2 is false.
C) Statement 1 is false and statement 2 is true.
D) Both statements are false.

## $\rightarrow$ Problem 3.1

The value of $K_{w}$ for water at $35^{\circ} \mathrm{C}$ is $10^{-12}$. If the pH of a solution at this temperature is 5.8 , is the solution acidic, basic, or neutral?
$\boldsymbol{\alpha})$ The solution is acidic.
$\boldsymbol{\beta})$ The solution is basic.
$\boldsymbol{\gamma})$ The solution is neutral.

## $\rightarrow$ Problem 3.2

Determine the pH of a solution of 0.001 M hydroiodic acid, HI .
A) $p \mathrm{H}=1$
B) $p \mathrm{H}=2$
C) $p \mathrm{H}=3$
D) $p \mathrm{H}=4$

## $\rightarrow$ Problem 3.3

Determine the pH of a solution of 0.001 M sulfuric acid, $\mathrm{H}_{2} \mathrm{SO}_{4}$.
A) $p \mathrm{H}=1.35$
B) $p \mathrm{H}=2.70$
C) $p \mathrm{H}=3.11$
D) $p \mathrm{H}=4.05$
$\rightarrow$ Problem 3.4
Determine the pH of a solution of 0.001 M sodium hydroxide, NaOH .
A) $p \mathrm{H}=11$
B) $p \mathrm{H}=12$
C) $p \mathrm{H}=13$
D) $p \mathrm{H}=13.5$
$\rightarrow$ Problem 3.5
Determine the pH of a solution of 0.001 M barium hydroxide, $\mathrm{Ba}(\mathrm{OH})_{2}$.
A) $\mathrm{pH}=10.1$
B) $\mathrm{pH}=11.3$
C) $p \mathrm{H}=12.1$
D) $p \mathrm{H}=13.3$

## $\rightarrow$ Problem 3.6

100 mL of 0.015 M HCl solution is mixed with 100 mL of 0.005 M HCl solution. The pH of the resultant solution is
A) $p \mathrm{H}=2.0$
B) $p \mathrm{H}=2.5$
C) $p \mathrm{H}=3.0$
D) $p \mathrm{H}=3.5$
$\rightarrow$ Problem 3.7
50 mL of an aqueous solution with pH equal to 1 . is mixed with 50 mL of a solution with pH equal to 1.5 . The pH of the resulting solution is most nearly:
A) $p \mathrm{H}=1.1$
B) $p \mathrm{H}=1.2$
C) $p \mathrm{H}=1.3$
D) $p \mathrm{H}=1.4$
$\rightarrow$ Problem 3.8
Determine the pH of a mixture of 250 mL 0.01 M HI and 250 mL 0.01 M
$\mathrm{H}_{2} \mathrm{SO}_{4}$.
A) $p \mathrm{H}=0.411$
B) $p \mathrm{H}=1.02$
C) $p \mathrm{H}=1.82$
D) $p \mathrm{H}=2.41$
$\rightarrow$ Problem 3.9
Determine the pH of a mixture of 400 mL 0.01 M NaOH and 200 mL 0.01 $\mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}$.
A) $p \mathrm{H}=8.82$
B) $p \mathrm{H}=9.51$
C) $p \mathrm{H}=10.9$
D) $p \mathrm{H}=12.1$
$\rightarrow$ Problem 3.10
Calculate the pH of a solution of 100 mL 0.2 M HI and 200 mL 0.1 M
NaOH .
A) $p \mathrm{H}=5.21$
B) $\mathrm{pH}=6.41$
C) $p \mathrm{H}=7.0$
D) $p \mathrm{H}=8.82$
$\rightarrow$ Problem 3.11
2 g of NaOH are added to 100 mL of $0.05 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ solution and the resulting solution is diluted with an additional 900 mL of water. The pH of the ensuing solution is:
A) $p \mathrm{H}=7.60$
B) $p \mathrm{H}=8.60$
C) $p \mathrm{H}=10.6$
D) $p \mathrm{H}=12.6$
$\rightarrow$ Problem 4.1
Calculate the pH of a 1 M solution of benzoic acid, given $K_{a}=6.46 \times 10^{-5}$.
A) $p \mathrm{H}=0.698$
B) $p \mathrm{H}=1.41$
C) $p \mathrm{H}=2.09$
D) $p \mathrm{H}=3.12$
$\rightarrow$ Problem 4.2
Calculate the pH of a $9.8 \times 10^{-5} \mathrm{M}$ solution of benzoic acid, given the same value of $K_{a}$ specified in the previous problem.
A) $p \mathrm{H}=4.27$
B) $p \mathrm{H}=5.35$
C) $p \mathrm{H}=6.12$
D) $p \mathrm{H}=6.52$

## $\rightarrow$ Problem 4.3

Calculate the pH of a 1 M solution of ammonia, given $K_{b}=1.78 \times 10^{-5}$.
A) $p \mathrm{H}=9.81$
B) $p \mathrm{H}=10.1$
C) $p \mathrm{H}=11.6$
D) $p \mathrm{H}=12.8$

## $\rightarrow$ Problem 4.4

Calculate the pH of a $9.8 \times 10^{-5} \mathrm{M}$ solution of ammonia, given the same value of $K_{b}$ specified in the previous problem.
A) $p \mathrm{H}=7.92$
B) $p \mathrm{H}=8.45$
C) $p \mathrm{H}=9.01$
D) $p \mathrm{H}=9.53$

## $\rightarrow$ Problem 5.1

A solution contains $0.1 \mathrm{M} \mathrm{H}_{2} \mathrm{~S}$ and 0.32 M HCl . Calculate the concentration of $\mathrm{HS}^{-}$and $\mathrm{S}^{2-}$ ions in solution, given the following dissociation constants.

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{~S}(\mathrm{aq}) \rightleftarrows \mathrm{HS}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) ; K_{a, 1}=1.0 \times 10^{-7} \\
& \mathrm{HS}^{-}(\mathrm{aq}) \rightleftarrows \mathrm{S}^{2-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) ; K_{a, 2}=1.3 \times 10^{-13}
\end{aligned}
$$

A) $\left[\mathrm{HS}^{-}\right]=3.13 \times 10^{-8} \mathrm{M}$ and $\left[\mathrm{S}^{2-}\right]=1.27 \times 10^{-20} \mathrm{M}$
B) $\left[\mathrm{HS}^{-}\right]=3.13 \times 10^{-8} \mathrm{M}$ and $\left[\mathrm{S}^{2-}\right]=1.27 \times 10^{-18} \mathrm{M}$
C) $\left[\mathrm{HS}^{-}\right]=3.13 \times 10^{-6} \mathrm{M}$ and $\left[\mathrm{S}^{2-}\right]=1.27 \times 10^{-20} \mathrm{M}$
D) $\left[\mathrm{HS}^{-}\right]=3.13 \times 10^{-6} \mathrm{M}$ and $\left[\mathrm{S}^{2-}\right]=1.27 \times 10^{-18} \mathrm{M}$
$\rightarrow$ Problem 5.2
Consider a solution of 0.01 M phosphoric acid, $\mathrm{H}_{3} \mathrm{PO}_{4}$, and the following chemical equilibria:

$$
\begin{gathered}
\mathrm{H}_{3} \mathrm{PO}_{4} \rightleftarrows \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} ; K_{1}=7 \times 10^{-3} \\
\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightleftarrows \mathrm{H}^{+}+\mathrm{HPO}_{4}^{2-} ; K_{2}=6.3 \times 10^{-8} \\
\mathrm{HPO}_{4}^{2-} \rightleftarrows \mathrm{H}^{+}+\mathrm{PO}_{4}^{3-} ; K_{3}=4.5 \times 10^{-13}
\end{gathered}
$$

True or false?
1.( ) The equilibrium concentration of phosphoric acid is greater than 0.004 M .
2.() The equilibrium concentration of dihydrogen phosphate ion is greater than 0.008 M .
3.( ) The equilibrium concentration of monohydrogen phosphate ion is greater than $5 \times 10^{-8} \mathrm{M}$.
4.( ) The equilibrium concentration of phosphate ion is greater than $10^{-16} \mathrm{M}$.
$\rightarrow$ Problem 6.1
A solution of equal concentrations of lactic acid and sodium lactate was found to have a $\mathrm{pH}=3.86$. Find the value of $K_{a}$ for lactic acid.
A) $K_{a}=1.38 \times 10^{-5}$
B) $K_{a}=6.35 \times 10^{-5}$
C) $K_{a}=1.38 \times 10^{-4}$
D) $K_{a}=6.35 \times 10^{-4}$

## $\rightarrow$ Problem 6.2

Reconsider the system introduced in the previous problem. What would the pH be if the concentration of acid were twice that of the salt?
A) $p \mathrm{H}=2.35$
B) $p \mathrm{H}=2.82$
C) $p \mathrm{H}=3.01$
D) $p \mathrm{H}=3.56$

## $\rightarrow$ Problem 6.3

Calculate the pH of a solution that is $0.50 \mathrm{M} \mathrm{Na}_{2} \mathrm{HSO}_{4}$ and $0.25 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$, given the following equilibrium constant.

$$
\mathrm{HSO}_{4}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq}) ; K_{a}=1.20 \times 10^{-2}
$$

A) $p \mathrm{H}=1.22$
B) $p \mathrm{H}=1.42$
C) $p \mathrm{H}=1.62$
D) $p \mathrm{H}=1.92$

## $\rightarrow$ Problem 6.4

Reconsider the system introduced in the previous problem. Calculate the pH of a solution that is $0.50 \mathrm{M} \mathrm{NaHSO}_{4}$ and $0.10 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$.
A) $p \mathrm{H}=1.22$
B) $p \mathrm{H}=1.42$
C) $p \mathrm{H}=1.62$
D) $p \mathrm{H}=1.92$

## $\rightarrow$ Problem 6.5

Reconsider the system introduced in Problem 6.3. Calculate the pH of a solution that is $0.50 \mathrm{M} \mathrm{NaHSO}_{4}$ and $0.50 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$.
A) $p \mathrm{H}=1.22$
B) $p \mathrm{H}=1.42$
C) $p \mathrm{H}=1.62$
D) $p \mathrm{H}=1.92$

## $\rightarrow$ Problem 6.6

A buffer solution of volume 100 mL is $0.1 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and 0.1 M $\mathrm{NaCH}_{3} \mathrm{CO}_{2}(\mathrm{aq})$. What is the pH after 10.0 mL of $0.950 \mathrm{M} \mathrm{NaOH}(\mathrm{aq})$ solution is added to this system? Use $p K_{a}=4.75$ for the HAc/Ac- pair.
A) $p \mathrm{H}=4.92$
B) $p \mathrm{H}=5.45$
C) $p \mathrm{H}=6.34$
D) $p \mathrm{H}=7.12$

## $\rightarrow$ Problem 6.7

What is the final pH after 20.0 mL of $0.1 \mathrm{M} \mathrm{HNO}_{3}(\mathrm{aq})$ solution is added to the system introduced in the previous problem?
A) $p \mathrm{H}=3.04$
B) $p \mathrm{H}=3.55$
C) $p \mathrm{H}=4.04$
D) $p \mathrm{H}=4.57$
$\rightarrow$ Problem 6.8
A buffer solution of volume 100 mL is $0.150 \mathrm{M} \mathrm{Na}_{2} \mathrm{HPO}_{4}(\mathrm{aq})$ and 0.100 M $\mathrm{KH}_{2} \mathrm{PO}_{4}(\mathrm{aq})$. What is the pH resulting from the addition of 80.0 mL of 0.01 M $\mathrm{NaOH}(\mathrm{aq})$ to the buffer solution? Use $p K_{a}=7.20$ for the $\mathrm{H}_{2} \mathrm{PO}_{4} / / \mathrm{HPO}_{4}{ }^{2-}$ pair.
A) $p \mathrm{H}=7.44$
B) $p \mathrm{H}=7.89$
C) $p \mathrm{H}=8.11$
D) $p \mathrm{H}=8.85$

## $\rightarrow$ Problem 6.9

What is the final pH after 10.0 mL of $1.0 \mathrm{M} \mathrm{HNO}_{3}(\mathrm{aq})$ solution is added to the system introduced in the previous problem?
A) $p \mathrm{H}=6.36$
B) $p \mathrm{H}=6.60$
C) $p \mathrm{H}=6.85$
D) $p \mathrm{H}=7.08$

## $\rightarrow$ Problem 7.1

How much volume of pure water needs to be added to 1 mL of a 0.1 M solution of a weak monobasic acid with $K_{a}=10^{-5}$ so as to increase its pH by one unit?
A) $+V=9 \mathrm{~mL}$
B) $+V=99 \mathrm{~mL}$
C) $+V=500 \mathrm{~mL}$
D) $+V=999 \mathrm{~mL}$

## $\rightarrow$ Problem 7.2

A current of 9.65 A is passed through 1 L of NaCl solution for 100 sec What will be the pH of the resulting solution? Assume $100 \%$ current efficiency and constancy of solution volume.
A) $p \mathrm{H}=1$
B) $p \mathrm{H}=2$
C) $p \mathrm{H}=3$
D) $p \mathrm{H}=4$

## $\rightarrow$ Problems 8.1-3

Determine the solubility products of salts silver bromide ( AgBr ), magnesium fluoride $\left(\mathrm{MgF}_{2}\right)$, and silver phosphate $\left(\mathrm{Ag}_{3} \mathrm{PO}_{4}\right)$, given their respective molar solubilities.

| Compound | Molar solubility (mol/L) |
| :---: | :---: |
| AgBr | $8.8 \times 10^{-7}$ |
| $\mathrm{MgF}_{2}$ | $1.2 \times 10^{-3}$ |
| $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ | $2.7 \times 10^{-6}$ |


| Compound 1: AgBr | Compound 2: $\mathrm{MgF}_{2}$ | Compound 3: $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ |
| :--- | :--- | :--- |
| A) $K_{s p}=7.74 \times 10^{-13}$ | A) $K_{s p}=6.91 \times 10^{-10}$ | A) $K_{s p}=6.43 \times 10^{-22}$ |
| B) $K_{s p}=1.24 \times 10^{-12}$ | B) $K_{s p}=1.12 \times 10^{-9}$ | B) $K_{s p}=1.43 \times 10^{-21}$ |
| C) $K_{s p}=7.74 \times 10^{-12}$ | C) $K_{s p}=6.91 \times 10^{-9}$ | C) $K_{s p}=6.43 \times 10^{-21}$ |
| D) $K_{s p}=1.24 \times 10^{-11}$ | D) $K_{s p}=1.12 \times 10^{-8}$ | D) $K_{3}=1.43 \times 10^{-20}$ |

## $\rightarrow$ Problems 8.4-6

Determine the molar solubilities of salts copper(I) chloride ( CuCl ), silver carbonate $\left(\mathrm{Ag}_{2} \mathrm{CO}_{3}\right)$, and bismuth(III) iodide $\left(\mathrm{Bil}_{3}\right)$, given their respective solubility products.

| Compound | Solubility Product |
| :---: | :---: |
| CuCl | $1.0 \times 10^{-6}$ |
| $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ | $8.46 \times 10^{-12}$ |
| $\mathrm{Bil}_{3}$ | $7.71 \times 10^{-19}$ |


| Compound 1: CuCl | Compound 2: $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ | Compound 3: $\mathrm{Bil}_{3}$ |
| :--- | :--- | :--- |
| A) $S=5.11 \times 10^{-5} \mathrm{M}$ | A) $S=5.26 \times 10^{-6} \mathrm{M}$ | A) $S=6.32 \times 10^{-6}$ |
| B) $S=1.0 \times 10^{-4} \mathrm{M}$ | B) $S=1.28 \times 10^{-5} \mathrm{M}$ | B) $S=1.30 \times 10^{-5}$ |
| C) $S=5.11 \times 10^{-4} \mathrm{M}$ | C) $S=5.26 \times 10^{-5} \mathrm{M}$ | C) $S=6.32 \times 10^{-5}$ |
| D) $S=1.0 \times 10^{-3} \mathrm{M}$ | D) $S=1.28 \times 10^{-4} \mathrm{M}$ | D) $S=1.30 \times 10^{-4}$ |

## $\rightarrow$ Problem 8.7

Calculate the solubility of silver chloride in a solution of $0.20 \mathrm{M} \mathrm{NaCl}(\mathrm{aq})$. The solubility product of AgCl is $1.6 \times 10^{-10}$.
A) $S=8.0 \times 10^{-10} \mathrm{M}$
B) $S=1.61 \times 10^{-9} \mathrm{M}$
C) $S=8.0 \times 10^{-9} \mathrm{M}$
D) $S=1.61 \times 10^{-8} \mathrm{M}$

## $\rightarrow$ Problem 8.8

Calculate the solubility of iron(II) hydroxide in a solution of 2.5 mM $\mathrm{FeCl}_{2}(\mathrm{aq})$. The solubility product of $\mathrm{Fe}(\mathrm{OH})_{2}$ is $1.6 \times 10^{-14}$.
A) $S=8.41 \times 10^{-7} \mathrm{M}$
B) $S=1.26 \times 10^{-6} \mathrm{M}$
C) $S=8.41 \times 10^{-6} \mathrm{M}$
D) $S=1.26 \times 10^{-5} \mathrm{M}$

## $\rightarrow$ Problem 8.9

Calculate the solubility of mercury $(\mathrm{I})$ chloride, $\mathrm{Hg}_{2} \mathrm{Cl}_{2}$, in a solution of 0.15 M $\mathrm{NaCl}(\mathrm{aq})$. The solubility product of $\mathrm{Hg}_{2} \mathrm{Cl}_{2}$ is $2.6 \times 10^{-18}$.
A) $S=1.16 \times 10^{-16} \mathrm{M}$
B) $S=8.82 \times 10^{-16} \mathrm{M}$
C) $S=1.16 \times 10^{-15} \mathrm{M}$
D) $S=8.82 \times 10^{-15} \mathrm{M}$

## $\rightarrow$ Problem 8.10

The solubility product constants of salts $M X, M X_{2}$ and $M_{3} X$ at a temperature $T$ are $4.0 \times 10^{-8}, 3.2 \times 10^{-14}$, and $2.7 \times 10^{-15}$, respectively. The solubilities of the salts at the temperature in question are in the order:
A) $M X>M X_{2}>M_{3} X$
B) $M_{3} X>M X_{2}>M X$
C) $M X_{2}>M_{3} X>M X$
D) $M X>M_{3} X>M X_{2}$

## $\rightarrow$ Problem 9.1

Find the molarity of $\mathrm{Ag}^{+}$ions required for the formation of a precipitate in $1.0 \times 10^{-5} \mathrm{M} \mathrm{NaCl}(\mathrm{aq})$, then answer: what mass of solid $\mathrm{AgNO}_{3}$ needs to be added for the onset of precipitation in 100 mL of this solution? The solubility product of AgCl is $1.6 \times 10^{-10}$.
A) $m=90.5 \mu \mathrm{~g} \mathrm{AgNO} 3$
B) $m=181 \mu \mathrm{~g} \mathrm{AgNO} 3$
C) $m=272 \mu \mathrm{~g} \mathrm{AgNO}_{3}$
D) $m=388 \mu \mathrm{~g} \mathrm{AgNO} 3$
$\rightarrow$ Problem 9.2
Determine the pH required for the onset of precipitation of $\mathrm{Ni}(\mathrm{OH})_{2}$ from a solution of $0.05 \mathrm{M} \mathrm{NiSO}_{4}$. The solubility product of $\mathrm{Ni}(\mathrm{OH})_{2}$ is $6.5 \times 10^{-18}$.
A) $p \mathrm{H}=6.06$
B) $p \mathrm{H}=7.23$
C) $p \mathrm{H}=8.81$
D) $p \mathrm{H}=9.50$

## $\rightarrow$ Problem 9.3

Suppose there are typically 20 average-sized drops in 1.0 mL of an aqueous solution. Will a precipitate form when 1 drop of $0.01 \mathrm{M} \mathrm{NaCl}(\mathrm{aq})$ is added to 10 mL of (1) $0.004 \mathrm{M} \mathrm{AgNO}_{3}$ or (2) $0.004 \mathrm{M} \mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ ? The solubility products of AgCl and $\mathrm{PbCl}_{2}$ are $1.6 \times 10^{-10}$ and $1.7 \times 10^{-5}$, respectively.
A) A precipitate will form in both (1) and (2).
B) A precipitate will form in (1), but not in (2).
C) A precipitate will form in (2), but not in (1).
D) A precipitate will not form in (1) and (2).

## $\rightarrow$ Problem 9.4

The concentrations of calcium, magnesium, and nickel(II) ions in an aqueous solution are $0.001 \mathrm{~mol} / \mathrm{L}$. In what order, first to last, do they precipitate when solid KOH is added? Refer to the following table for the pertinent solubility products.

| Compound | $\boldsymbol{K}_{\boldsymbol{s p}}$ |
| :---: | :---: |
| $\mathrm{Ca}(\mathrm{OH})_{2}$ | $5.5 \times 10^{-6}$ |
| $\mathrm{Mg}(\mathrm{OH})_{2}$ | $1.1 \times 10^{-11}$ |
| $\mathrm{Ni}(\mathrm{OH})_{2}$ | $6.5 \times 10^{-18}$ |

A) $\mathrm{Mg}(\mathrm{OH})_{2}, \mathrm{Ni}(\mathrm{OH})_{2}, \mathrm{Ca}(\mathrm{OH})_{2}$
B) $\mathrm{Ca}(\mathrm{OH})_{2}, \mathrm{Mg}(\mathrm{OH})_{2}, \mathrm{Ni}(\mathrm{OH})_{2}$
C) $\mathrm{Ni}(\mathrm{OH})_{2}, \mathrm{Mg}(\mathrm{OH})_{2}, \mathrm{Ca}(\mathrm{OH})_{2}$
D) $\mathrm{Ni}(\mathrm{OH})_{2}, \mathrm{Ca}(\mathrm{OH})_{2}, \mathrm{Mg}(\mathrm{OH})_{2}$

## $\rightarrow$ Problem 9.5

Reconsider the previous problem. Find the pH at which each salt will begin to precipitate.

## SOLUTIONS

## P. $1 \Rightarrow$ Solution

Part 1: As usual, we begin by drawing up a concentration diagram.

| Conc. | $\mathrm{N}_{2} \mathrm{H}_{4}$ | $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{N}_{2} \mathrm{H}_{5}{ }^{+}$ | $\mathrm{OH}^{-}$ |
| :---: | :---: | :---: | :---: | :---: |
| Initial | $C$ | - | 0 | 0 |
| Change | $-C \alpha$ | - | $+C \alpha$ | $+C \alpha$ |
| Final | $C(1-\alpha)$ | - | $C \alpha$ | $C \alpha$ |

From the law of mass action, we have

$$
K_{b}=\frac{C \alpha \times C \alpha}{C(1-\alpha)}=\frac{C \alpha^{2}}{1-\alpha}
$$

Since $1-\alpha \approx 1$, the equation simplifies to

$$
K_{b}=\frac{C \alpha^{2}}{1-\alpha} \approx C \alpha^{2}
$$

The initial concentration $C$ of aniline in the solution is

$$
C=\frac{0.32}{32 \times 0.5}=0.02 \mathrm{M}
$$

so that, substituting in the foregoing equation and solving for $\alpha$, we obtain

$$
\begin{gathered}
K_{b}=C \alpha^{2} \rightarrow \alpha=\left(\frac{K_{b}}{C}\right)^{1 / 2} \\
\therefore \alpha=\left(\frac{3.6 \times 10^{-6}}{0.02}\right)^{1 / 2}=0.0134=1.34 \%
\end{gathered}
$$

- The correct answer is $\mathbf{B}$.

Part 2: Applying a concentration balance to this system should yield the same result from Problem 1.1, namely

$$
K_{a}=\frac{C \alpha^{2}}{1-\alpha}
$$

which, in view of the approximation $1-\alpha \approx 1$, becomes

$$
K_{a} \approx C \alpha^{2}
$$

Solving for $\alpha$ and substituting, we obtain

$$
\begin{gathered}
K_{a}=C \alpha^{2} \rightarrow \alpha=\left(\frac{K_{a}}{C}\right)^{1 / 2} \\
\therefore \alpha=\left(\frac{1.6 \times 10^{-5}}{0.08}\right)^{1 / 2}=0.0141=1.41 \%
\end{gathered}
$$

- The correct answer is $\mathbf{C}$.


## P. $2 \Rightarrow$ Solution

Part 1: Placing the water in contact with atmospheric air causes the concentration of $\mathrm{CO}_{2}$ to increase, displacing the carbon dioxide-water equilibrium to the right and promoting the formation of $\mathrm{H}^{+}$ions. As a result, the solution will be acidified and the indicator will turn yellow.

- The correct answer is $\boldsymbol{\alpha}$.

Part 2: 1. True. The main constituent of vinegar is acetic acid. Accordingly, placing the indicator in contact with acetic acid, a pH -reducing substance, should cause the indicator solution to turn yellow.
2. False. Ammonia is a base, and as such should increase the pH of the solution and turn the indicator solution blue.
3.True. Sodium acetate originates from a weak acid and a strong base, and hence should increase the pH of the solution and turn the indicator blue.
4.False. Since sodium chloride originates from a strong acid and a strong base, it should produce no effect on the pH of the solution. The indicator should remain green.

Part 3: One of the main components of lemon juice is citric acid. The results from experiment 1 indicate that, when the indicator is placed in contact with an acid environment (since in this experiment there is more HCl than NaOH ), it will turn yellow. Adding the mixture of experiment 1 with that of experiment 2 would produce a system with $2+2=4 \mathrm{~mL}$ of HCl and $1+3=4 \mathrm{~mL}$ of NaOH , producing a neutral solution. The indicator solution should turn green.

- The correct answer is B.


## P. $3 \rightarrow$ Solution

Part 1: The reference concentration of $\mathrm{H}^{+}$at this temperature is

$$
\begin{aligned}
K_{w}= & {\left[\mathrm{H}^{+}\right]^{2} \rightarrow 10^{-12}=\left[\mathrm{H}^{+}\right]^{2} } \\
& \therefore\left[\mathrm{H}^{+}\right]=10^{-6} \mathrm{M}
\end{aligned}
$$

Accordingly, the solution should be acidic if $\mathrm{pH}<6$, basic if $\mathrm{pH}>6$, and neutral if $\mathrm{pH}=6$. A solution with $\mathrm{pH}=5.8$ is clearly acidic.

- The correct answer is $\boldsymbol{\alpha}$.

Part 2: Assuming hydroiodic acid dissociates completely, we have $\left[\mathrm{H}^{+}\right]=$ 0.001 M . The pH of the solution is then

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log (0.001)=3
$$

- The correct answer is C.

Part 3: Assuming sulfuric acid dissociates completely, we have $\left[\mathrm{H}^{+}\right]=2 \times$ $0.001=0.002 \mathrm{M}$. The pH of the solution is then

$$
\mathrm{pH}=-\log (0.002)=2.70
$$

- The correct answer is $\mathbf{B}$.

Part 4: Assuming sodium hydroxide dissociates completely, we have $\left[\mathrm{OH}^{-}\right]$ $=0.001 \mathrm{M}$. The concentration of $\mathrm{H}^{+}$ions follows from the ionic product of water,

$$
\begin{gathered}
{\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=10^{-14} \rightarrow\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{\left[\mathrm{OH}^{-}\right]}} \\
\therefore\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{0.001}=10^{-11}
\end{gathered}
$$

The pH is then

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(10^{-11}\right)=11
$$

- The correct answer is A.

Part 5: Assuming barium hydroxide dissociates completely, we have $\left[\mathrm{OH}^{-}\right]=$ $2 \times 0.001=0.002 \mathrm{M}$. The concentration of $\mathrm{H}^{+}$ions follows from the ionic product of water,

$$
\begin{gathered}
{\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=10^{-14} \rightarrow\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{\left[\mathrm{OH}^{-}\right]}} \\
\therefore\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{0.002}=5 \times 10^{-12} \mathrm{M}
\end{gathered}
$$

The pH is then

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(5 \times 10^{-12}\right)=11.3
$$

- The correct answer is $\mathbf{B}$.

Part 6: From the 0.015 M solution, we have $0.1 \times 0.015=0.0015 \mathrm{~mol}$ of $\mathrm{H}^{+}$ions. From the 0.005 M solution, in turn, we have $0.1 \times 0.005=5 \times 10^{-4} \mathrm{~mol}$ of $\mathrm{H}^{+}$ions. The total volume of the final solution is $0.1+0.1=0.2 \mathrm{~L}$, and the concentration of hydronium ions follows as

$$
\left[\mathrm{H}^{+}\right]=\frac{0.0015+5 \times 10^{-4}}{0.2}=0.01 \mathrm{M}
$$

Lastly, the pH of the ensuing solution is

$$
p \mathrm{H}=-\log \left[\mathrm{H}^{+}\right]=-\log (0.01)=2
$$

- The correct answer is A.

Part 7: The concentration of hydronium ions in the solution with $\mathrm{pH}=1$ is $\left[\mathrm{H}^{+}\right]=10^{-1} \mathrm{M}$, and the amount of such ions contained in 50 mL of solution is $0.05 \times$ $10^{-1}=0.005 \mathrm{~mol}$. Similarly, the amount of $\mathrm{H}^{+}$ions in 50 mL of the other solution is $0.05 \times 10^{-1.5}=0.00158 \mathrm{~mol}$. Then, the total amount of $\mathrm{H}^{+}$ions in the mixed solution is $0.005+0.00158=0.00658 \mathrm{~mol}$, and the concentration is

$$
\left[\mathrm{H}^{+}\right]=\frac{0.00658}{0.05+0.05}=0.0658 \mathrm{M}
$$

Finally, the pH of the solution is

$$
p \mathrm{H}=-\log \left[\mathrm{H}^{+}\right]=-\log (0.0658)=1.18 \approx 1.2
$$

- The correct answer is $\mathbf{B}$.

Part 8: The number of moles of $\mathrm{H}^{+}$ions from HI is $0.25 \times 0.01=0.0025$ mol , and the number of moles of $\mathrm{H}^{+}$ions from $\mathrm{H}_{2} \mathrm{SO}_{4}$ is $0.25 \times 2 \times 0.01=0.005$ mol. Given the final volume $V=0.25+0.25=0.5 \mathrm{~L},\left[\mathrm{H}^{+}\right]$is calculated as

$$
\left[\mathrm{H}^{+}\right]=\frac{0.0025+0.005}{0.5}=0.015 \mathrm{M}
$$

The corresponding pH is then

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log (0.015)=1.82
$$

- The correct answer is $\mathbf{C}$.

Part 9: The number of moles of $\mathrm{OH}^{-}$ions from NaOH is $0.4 \times 0.01=0.004$ mol , and the number of moles of $\mathrm{H}^{+}$ions from $\mathrm{Ba}(\mathrm{OH})_{2}$ is $0.2 \times 2 \times 0.01=0.004$ mol. Given the final volume $V=0.4+0.2=0.6 \mathrm{~L}$, the concentration of $\left[\mathrm{OH}^{-}\right]$ions is determined as

$$
\left[\mathrm{OH}^{-}\right]=\frac{0.004+0.004}{0.6}=0.0133 \mathrm{M}
$$

The concentration of $\mathrm{H}^{+}$ions follows from the ionic product of water,

$$
\begin{gathered}
K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right] \rightarrow\left[\mathrm{H}^{+}\right] \times 0.0133=10^{-14} \\
\therefore\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{0.0133}=7.52 \times 10^{-13}
\end{gathered}
$$

Finally, the pH of the solution is

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(7.52 \times 10^{-13}\right)=12.1
$$

- The correct answer is $\mathbf{D}$.

Part 10: The number of moles of $\mathrm{H}^{+}$ions from hydroiodic acid solution is $0.1 \times 0.2=0.02 \mathrm{~mol}$, while the number of moles of $\mathrm{OH}^{-}$ions from sodium hydroxide is $0.2 \times 0.1=0.02 \mathrm{~mol}$. Since the amounts of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$added to the solution are equal, there is no excess of either ion and the solution should be neutral, with a pH of 7 .

## - The correct answer is $\mathbf{C}$.

Part 11: 2 g of NaOH corresponds to $2 / 40=0.05 \mathrm{~mol}^{2} \mathrm{OH}^{-}$. In turn, 100 mL of the $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution corresponds to $2 \times 0.05 \times 0.1=0.01 \mathrm{~mol}$ of $\mathrm{H}^{+}$. Clearly, there is an excess $0.05-0.01=0.04$ mol of hydroxyl ions, and the concentration of $\mathrm{OH}^{-}$once the solution is diluted is $0.04 / 1.0=0.04 \mathrm{M}$. The pOH is

$$
p \mathrm{OH}=-\log \left[\mathrm{OH}^{-}\right]=-\log (0.04)=1.40
$$

and the corresponding pH follows as

$$
p \mathrm{H}=14-p \mathrm{OH}=14-1.40=12.6
$$

- The correct answer is $\mathbf{D}$.


## P. $4 \Rightarrow$ Solution

Part 1: Since the acid in question is weak, the concentration of $\mathrm{H}^{+}$ion can be determined with Ostwald's dilution law. The percentage dissociation $\alpha$ is given by

$$
K_{a}=C \alpha^{2}
$$

However, $\left[\mathrm{H}^{+}\right]=C \alpha$, so

$$
\begin{gathered}
{\left[\mathrm{H}^{+}\right]=C \alpha=C \times \sqrt{\frac{K_{a}}{C}}=\sqrt{K_{a} C}} \\
\therefore\left[\mathrm{H}^{+}\right]=\sqrt{\left(6.46 \times 10^{-5}\right) \times 1}=8.04 \times 10^{-3} \mathrm{M}
\end{gathered}
$$

The corresponding pH is

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(8.04 \times 10^{-3}\right)=2.09
$$

- The correct answer is C.

Part 2: Since the concentration of benzoic acid is now of the same order of magnitude as $K_{a}$, the complete form of Ostwald's dilution law must be employed. That is,

$$
\begin{aligned}
& K_{a}=\frac{C \alpha^{2}}{1-\alpha} \rightarrow 6.46 \times 10^{-5}=\frac{\left(9.8 \times 10^{-5}\right) \times \alpha^{2}}{1-\alpha} \\
& \therefore 6.46 \times 10^{-5}-6.46 \times 10^{-5} \alpha=\left(9.8 \times 10^{-5}\right) \times \alpha^{2} \\
& \therefore 9.8 \times 10^{-5} \alpha^{2}+6.46 \times 10^{-5} \alpha-6.46 \times 10^{-5}=0
\end{aligned}
$$

Solving the quadratic equation above gives $\alpha=0.547$. The concentration of $\mathrm{H}^{+}$follows as

$$
\left[\mathrm{H}^{+}\right]=C \alpha=\left(9.8 \times 10^{-5}\right) \times 0.547=5.36 \times 10^{-5} \mathrm{M}
$$

and the corresponding pH is

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(5.36 \times 10^{-5}\right)=4.27
$$

- The correct answer is $\mathbf{A}$.

Part 3: The concentration of hydroxyl ions is

$$
\left[\mathrm{OH}^{-}\right]=\sqrt{K_{b} C}=\sqrt{\left(1.78 \times 10^{-5}\right) \times 1.0}=0.00422 \mathrm{M}
$$

With reference to the ionic product of water, the concentration of $\mathrm{H}^{+}$ions is

$$
\begin{aligned}
K_{w}= & {\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right] \rightarrow 10^{-14}=\left[\mathrm{H}^{+}\right] \times 0.00422 } \\
& \therefore\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{0.00422}=2.37 \times 10^{-12} \mathrm{M}
\end{aligned}
$$

Finally, the solution pH is

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(2.37 \times 10^{-12}\right)=11.6
$$

- The correct answer is $\mathbf{C}$.

Part 4: Observing that the concentration of ammonia is of the same order of magnitude as $K_{b}$, we should make use of the complete form of Ostwald's dilution law. Namely,

$$
\begin{aligned}
& K_{b}=\frac{C \alpha^{2}}{1-\alpha} \rightarrow 1.78 \times 10^{-5}=\frac{\left(9.8 \times 10^{-5}\right) \times \alpha^{2}}{1-\alpha} \\
& \therefore 1.78 \times 10^{-5}-1.78 \times 10^{-5} \alpha=\left(9.8 \times 10^{-5}\right) \times \alpha^{2} \\
& \therefore\left(9.8 \times 10^{-5}\right) \times \alpha^{2}+1.78 \times 10^{-5} \alpha-1.78 \times 10^{-5}
\end{aligned}
$$

Solving the quadratic equation above gives $\alpha=0.345$. The concentration of $\mathrm{OH}^{-}$follows as

$$
\left[\mathrm{OH}^{-}\right]=C \alpha=\left(9.8 \times 10^{-5}\right) \times 0.345=3.38 \times 10^{-5} \mathrm{M}
$$

so that

$$
p \mathrm{OH}=-\log \left[\mathrm{OH}^{-}\right]=-\log \left(3.38 \times 10^{-5}\right)=4.47
$$

and

$$
p \mathrm{H}=14-p \mathrm{OH}=14-4.47=9.53
$$

- The correct answer is D.


## P. $5 \Rightarrow$ Solution

Part 1: Due to the common ion effect, we can take the $\mathrm{H}^{+}$ion concentration to be equal to the concentration of HCl ; that is, $\left[\mathrm{H}^{+}\right] \approx[\mathrm{HCl}]=0.32 \mathrm{M}$. Then, the concentration of bisulfide ions can be determined with the law of mass action,

$$
\begin{aligned}
& K_{a, 1}=\frac{\left[\mathrm{HS}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]} \rightarrow\left[\mathrm{HS}^{-}\right]=\frac{\left[\mathrm{H}_{2} \mathrm{~S}\right] \times K_{a, 1}}{\left[\mathrm{H}^{+}\right]} \\
& \therefore\left[\mathrm{HS}^{-}\right]=\frac{0.1 \times\left(1.0 \times 10^{-7}\right)}{0.32}=3.13 \times 10^{-8} \mathrm{M}
\end{aligned}
$$

Now, the dissociation constants for the acid in question can be expressed as

$$
K_{a, 1}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{HS}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]}=1.0 \times 10^{-7}
$$

and

$$
K_{a, 2}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{S}^{2-}\right]}{\left[\mathrm{HS}^{-}\right]}=1.3 \times 10^{-13}
$$

Multiplying one equation by the other and solving for $\left[\mathrm{S}^{2-}\right]$, we get

$$
\begin{gathered}
K_{a, 1} \times K_{a, 2}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{HS}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]} \times \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{S}^{2-}\right]}{\left[\mathrm{HS}^{-}\right]}=\left(1.0 \times 10^{-7}\right) \times\left(1.3 \times 10^{-13}\right) \\
\therefore \frac{\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{~S}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]}=1.3 \times 10^{-20} \\
\therefore \frac{0.32^{2} \times\left[\mathrm{S}^{2-}\right]}{0.1}=1.3 \times 10^{-20} \\
\therefore\left[\mathrm{~S}^{2-}\right]=\frac{\left(1.3 \times 10^{-20}\right) \times 0.1}{0.32^{2}}=1.27 \times 10^{-20} \mathrm{M}
\end{gathered}
$$

- The correct answer is A.

Part 2: We begin by assuming that most $\mathrm{H}^{+}$comes from the first dissociation, which is associated with the greatest $K$. If $\left[\mathrm{H}^{+}\right]=\left[\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{2-}\right]=x$, then $\left[\mathrm{H}_{3} \mathrm{PO}_{4}\right]=1-x$ and

$$
\begin{gathered}
K_{1}=\frac{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{2-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}_{3} \mathrm{PO}_{4}\right]} \rightarrow \frac{x \times x}{0.01-x}=7.0 \times 10^{-3} \\
\therefore \frac{x^{2}}{0.01-x}=7.0 \times 10^{-3} \\
\therefore x^{2}=\left(7.0 \times 10^{-3}\right) \times 0.01-7.0 \times 10^{-3} x \\
\therefore x^{2}+7.0 \times 10^{-3} x-7.0 \times 10^{-5}=0
\end{gathered}
$$

Solving the quadratic equation above gives $x=0.00557$. It follows that the equilibrium concentrations of hydronium ion, dihydrogen phosphate ion, and phosphoric acid are $\left[\mathrm{H}^{+}\right]=0.00557 \mathrm{M},\left[\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{2-}\right]=0.00557 \mathrm{M}$, and $\left[\mathrm{H}_{3} \mathrm{PO}_{4}\right]=0.01$
$-x=0.00443 \mathrm{M}$, respectively. With reference to the second equilibrium, we can establish the equilibrium concentration of monohydrogen phosphate ion,

$$
\begin{aligned}
& K_{2}=\frac{\left[\mathrm{HPO}_{4}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]} \rightarrow\left[\mathrm{HPO}_{4}^{-}\right]=\frac{K_{2} \times\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}{\left[\mathrm{H}^{+}\right]} \\
& \therefore\left[\mathrm{HPO}_{4}^{-}\right]=\frac{\left(6.3 \times 10^{-8}\right) \times 0.00557}{0.00557}=6.3 \times 10^{-8} \mathrm{M}
\end{aligned}
$$

Note that the concentration of $\mathrm{HPO}_{4}^{-}$is less than $0.001 \%$ of the concentration of dihydrogen phosphate, therefore our assumption that all $\mathrm{H}^{+}$comes from the first dissociation stage is indeed reasonable. Considering the third and last dissociation stage, we can determine the concentration of phosphate ion,

$$
\begin{aligned}
K_{3} & =\frac{\left[\mathrm{PO}_{4}^{3-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{HPO}_{4}^{2-}\right]} \rightarrow\left[\mathrm{PO}_{4}^{3-}\right]=\frac{K_{3} \times\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}^{+}\right]} \\
\therefore\left[\mathrm{PO}_{4}^{3-}\right]= & \frac{\left(4.5 \times 10^{-13}\right) \times\left(6.3 \times 10^{-8}\right)}{0.00557}=5.09 \times 10^{-18} \mathrm{M}
\end{aligned}
$$

- Statements $\mathbf{1}$ and $\mathbf{3}$ are true, whereas statements $\mathbf{2}$ and $\mathbf{4}$ are false.


## P. $6 \Rightarrow$ Solution

Part 1: From the Henderson-Hasselbalch equation, we have

$$
p K_{a}=p \mathrm{H}-\log \frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

However, with $\left[A^{-}\right]=[H A]$, the equation simplifies to

$$
\begin{gathered}
p K_{a}=p \mathrm{H}-\log \frac{[\mathrm{A}]}{[\mathrm{HA}]} \rightarrow p K_{a}=p \mathrm{H} \\
\therefore p K_{a}=3.86 \\
\therefore K_{a}=10^{-3.86}=1.38 \times 10^{-4}
\end{gathered}
$$

- The correct answer is C

Part 2: Let $x$ denote the concentration of lactate ion, $\left[L^{-}\right]$, and $y$ denote the concentration of hydronium. We prepare the following concentration diagram.

| Conc. | $\mathrm{HL}(\mathrm{aq})$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ | $\mathrm{L}^{-}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: |
| Initial | $2 x$ | - | - |  |
| Change | $-y$ | - | $+y$ | $+y$ |
| Equilibrium | $2 x-y$ | - | $y$ | $y+x$ |

Given $K_{a}=1.38 \times 10^{-4}$, we have

$$
K_{a}=\frac{\left[\mathrm{L}^{-}\right]\left[\mathrm{H}^{+}\right]}{[\mathrm{HL}]} \rightarrow \frac{(y+x) y}{2 x-y}=1.38 \times 10^{-4}
$$

Since lactic acid is a weak acid, we can surmise that $x \gg y$ and simplify, giving

$$
\begin{gathered}
\frac{(y+x) y}{2 x-y} \approx \frac{x y}{2 x}=1.38 \times 10^{-4} \\
\therefore \frac{y}{2}=1.38 \times 10^{-4} \\
\therefore y=2.76 \times 10^{-4} \mathrm{M}=\left[\mathrm{H}^{+}\right]
\end{gathered}
$$

Lastly, the solution pH is

$$
p \mathrm{H}=-\log \left(2.76 \times 10^{-4}\right)=3.56
$$

- The correct answer is $\mathbf{D}$.

Part 3: The $p K_{a}$ for the $\mathrm{HSO}_{4}-/ \mathrm{SO}_{4}{ }^{2-}$ reaction pair is $p K_{a}=-\log \left(1.20 \times 10^{-2}\right)$ $=1.92$. Since $\mathrm{HSO}_{4}^{-}$and $\mathrm{SO}_{4}{ }^{2-}$ are conjugated acid and base, the pH can be determined with the Henderson-Hasselbalch equation,

$$
p \mathrm{H}=p \mathrm{~K}_{a}+\log \frac{[\text { base }]}{[\text { acid }]}=1.92+\log \left(\frac{0.25}{0.5}\right)=1.62
$$

- The correct answer is C.

Part 4: The $p K_{a}$ continues to be 1.92, and the pH becomes

$$
p \mathrm{H}=1.92+\log \left(\frac{0.1}{0.5}\right)=1.22
$$

- The correct answer is $\mathbf{A}$.

Part 5: In this case, the second term in the HH equation equals zero and we have simply

$$
p \mathrm{H}=p K_{a}+\log \frac{[\text { base }]}{[\text { acid }]}=1.92
$$

- The correct answer is D.

Part 6: The initial pH is

$$
p \mathrm{H}=p \mathrm{~K}_{a}+\log \frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}=4.75+\log \left(\frac{0.1}{0.1}\right)=4.75
$$

The initial amounts of acetic acid and acetate ion are, respectively,

$$
\begin{aligned}
& n\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=0.1 \times 0.1=0.01 \mathrm{~mol} \\
& n\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)=0.1 \times 0.1=0.01 \mathrm{~mol}
\end{aligned}
$$

The amount of NaOH added, in turn, is $0.01 \times 0.950=9.5 \times 10^{-3} \mathrm{~mol}$, and should be followed by the production of $9.5 \times 10^{-3} \mathrm{~mol}^{\circ} \mathrm{CH}_{3} \mathrm{COO}^{-}$from acetic acid. The new concentrations of the two conjugate species are

$$
\begin{gathered}
{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=\frac{0.01-9.5 \times 10^{-3}}{0.110}=4.54 \times 10^{-3} \mathrm{M}} \\
{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=\frac{0.01+9.5 \times 10^{-3}}{0.110}=0.177 \mathrm{M}}
\end{gathered}
$$

and the updated pH is determined as

$$
p \mathrm{H}=4.75+\log \left(\frac{0.177}{4.54 \times 10^{-3}}\right)=6.34
$$

- The correct answer is C.

Part 7: An amount of $0.02 \times 0.1=0.002 \mathrm{~mol}$ of $\mathrm{HNO}_{3}$ is added to the system, and translates into an increase of 0.002 mol acetic acid from $\mathrm{CH}_{3} \mathrm{COO}^{-}$. Once nitric acid is added, the new concentrations of the two conjugate species become

$$
\begin{gathered}
{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=\frac{0.01+0.002}{0.120}=0.1 \mathrm{M}} \\
{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=\frac{0.01-0.002}{0.120}=0.0667 \mathrm{M}}
\end{gathered}
$$

and the updated pH is

$$
p \mathrm{H}=4.75+\log \left(\frac{0.0667}{0.1}\right)=4.57
$$

- The correct answer is $\mathbf{D}$.

Part 8: The initial pH is

$$
p \mathrm{H}=p \mathrm{~K}_{a}+\log \frac{\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}=7.20+\log \left(\frac{0.150}{0.100}\right)=7.38
$$

The initial amounts of dihydrogen phosphate and hydrogen phosphate are, respectively,

$$
\begin{gathered}
n\left(\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right)=0.1 \times 0.1=0.01 \mathrm{~mol} \\
n\left(\mathrm{HPO}_{4}^{2-}\right)=0.1 \times 0.15=0.015 \mathrm{~mol}
\end{gathered}
$$

The amount of NaOH added, in turn, is $0.08 \times 0.01=8 \times 10^{-4} \mathrm{~mol}$, and should be accompanied by the formation of an additional $8 \times 10^{-4} \mathrm{~mol}$ hydrogen phosphate from $\mathrm{Na}_{2} \mathrm{HPO}_{4}$. The new concentrations of the two conjugate species are

$$
\begin{aligned}
& {\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]=\frac{0.01-8 \times 10^{-4}}{0.18}=0.0511 \mathrm{M}} \\
& {\left[\mathrm{HPO}_{4}^{2-}\right]=\frac{0.015+8 \times 10^{-4}}{0.18}=0.0878 \mathrm{M}}
\end{aligned}
$$

and the updated pH follows as

$$
p \mathrm{H}=p \mathrm{~K}_{a}+\log \frac{\left[\mathrm{HPO}_{4}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]}=7.20+\log \left(\frac{0.0878}{0.0511}\right)=7.44
$$

- The correct answer is $\mathbf{A}$.

Part 9: An amount of $0.01 \times 1.0=0.01 \mathrm{~mol}$ of $\mathrm{HNO}_{3}$ is added to the system, and translates into an increase of 0.01 mol dihydrogen phosphate from $\mathrm{KH}_{2} \mathrm{PO}_{4}$. Once nitric acid is added, the new concentrations of the two conjugate species become

$$
\begin{gathered}
{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]=\frac{0.01+0.01}{0.110}=0.182 \mathrm{M}} \\
{\left[\mathrm{HPO}_{4}^{2-}\right]=\frac{0.015-0.01}{0.110}=0.0455 \mathrm{M}}
\end{gathered}
$$

and the updated pH is

$$
p \mathrm{H}=7.20+\log \left(\frac{0.0455}{0.182}\right)=6.60
$$

- The correct answer is $\mathbf{B}$.


## P. $7 \Rightarrow$ Solution

Part 1: The value of $p K_{a}=5$. The pH before dilution is given by

$$
p \mathrm{H}=\frac{1}{2}\left(p K_{a}-\log C\right)=\frac{1}{2} \times(5+1)=3
$$

For the pH to be raised by one unit, we must have

$$
\begin{gathered}
p \mathrm{H}=4 \rightarrow \frac{1}{2}\left(p K_{a}-\log C\right)=4 \\
\therefore \frac{1}{2} \times(5-\log C)=4 \\
\therefore 5-\log C=8 \\
\therefore \log C=-3
\end{gathered}
$$

or, equivalently, $C=10^{-3} \mathrm{M}$. The molarity must be decreased 100 times relatively to the initial value of 0.1 M ; this can be done by diluting the solution to 100 times its initial volume of 1 mL , that is, by adding 99 mL of water to the system.

- The correct answer is $\mathbf{B}$.

Part 2: The total charge passed through the solution is $9.65 \times 100=965$ C. In the cell in question, the anodic reaction is

$$
2 \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_{2}+2 e^{-}
$$

while the cathodic reaction is

$$
2 \mathrm{H}^{+}+2 e^{-} \rightarrow \mathrm{H}_{2}
$$

Thus, one mole of hydronium ions should be consumed for every mole of electrons, or $96,500 \mathrm{C}$. The number of moles of $\mathrm{H}^{+}$consumed for a charge of 965 C is straightforwardly obtained as

$$
\frac{1 \mathrm{~mol} \mathrm{H}^{+}}{96,500 \mathrm{C}}=\frac{x}{965 \mathrm{C}} \rightarrow x=0.01 \mathrm{molH}^{+}
$$

Since $\mathrm{H}^{+}$is converted into gas and leaves the solution, the concentration of hydroxyl ions should increase correspondingly; the final concentration of $\mathrm{OH}^{-}$is $\left[\mathrm{OH}^{-}\right]=0.01 / 1=0.01 \mathrm{M}$, and the $\mathrm{pOH}=12$. The final pH is then

$$
p \mathrm{H}=14-p \mathrm{OH}=14-12=2
$$

- The correct answer is $\mathbf{B}$.


## P. $8 \Rightarrow$ Solution

Part 1: The concentrations of $\mathrm{Ag}^{+}$and $\mathrm{Br}^{-}$are $\left[\mathrm{Ag}^{+}\right]=S=8.8 \times 10^{-7} \mathrm{M}$ and $\left[\mathrm{Br}^{-}\right]=S=8.8 \times 10^{-7} \mathrm{M}$, respectively. The solubility product is then

$$
K_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Br}^{-}\right]=\left(8.8 \times 10^{-7}\right) \times\left(8.8 \times 10^{-7}\right)=7.74 \times 10^{-13}
$$

- The correct answer is $\mathbf{A}$.

Part 2: The concentrations of $\mathrm{Mg}^{2+}$ and $\mathrm{F}^{-}$are $\left[\mathrm{Mg}^{2+}\right]=S=1.2 \times 10^{-3} \mathrm{M}$ and $\left[\mathrm{F}^{-}\right]=2 S=2.4 \times 10^{-3} \mathrm{M}$, respectively. The solubility product is then
$K_{\mathrm{sp}}=\left[\mathrm{Mg}^{2+}\right]\left[\mathrm{F}^{-}\right]^{2}=\left(1.2 \times 10^{-3}\right) \times\left(2.4 \times 10^{-3}\right)^{2}=6.91 \times 10^{-9}$

- The correct answer is $\mathbf{C}$.

Part 3: The concentrations of $\mathrm{Ag}^{+}$and $\mathrm{PO}_{4}{ }^{3-}$ are $\left[\mathrm{Ag}^{+}\right]=3 \mathrm{~S}=8.1 \times 10^{-6}$ $\mathrm{mol} / \mathrm{L}$ and $\left[\mathrm{PO}_{4}^{3-}\right]=S=2.7 \times 10^{-6} \mathrm{~mol} / \mathrm{L}$, respectively. The solubility product is then $K_{\text {sp }}=\left[\mathrm{Ag}^{+}\right]^{3}\left[\mathrm{PO}_{4}^{3-}\right]=\left(8.1 \times 10^{-6}\right)^{3} \times\left(2.7 \times 10^{-6}\right)=1.43 \times 10^{-21}$

- The correct answer is $\mathbf{B}$.

Part 4: Let $S$ denote the molar solubility of CuCl . Given $K_{s p}=1.0 \times 10^{-6}$, we have

$$
\begin{gathered}
K_{s p}=1.0 \times 10^{-6}=\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{Cl}^{-}\right]=S \times S=S^{2} \\
\therefore S=\left(1.0 \times 10^{-6}\right)^{1 / 2}=1.0 \times 10^{-3} \mathrm{M}
\end{gathered}
$$

- The correct answer is D.

Part 5: Let $S$ denote the molar solubility of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$. Given $K_{s p}=8.46 \times 10^{-}$ ${ }^{12}$, we have

$$
\begin{gathered}
K_{s p}=8.46 \times 10^{-12}=\left[\mathrm{Ag}^{+}\right]^{2}\left[\mathrm{CO}_{3}^{2-}\right]=(2 S)^{2} \times S=4 S^{3} \\
\therefore S=\left(\frac{8.46 \times 10^{-12}}{4}\right)^{1 / 3}=1.28 \times 10^{-4} \mathrm{M}
\end{gathered}
$$

- The correct answer is $\mathbf{D}$.

Part 6: Let $S$ denote the molar solubility of $\mathrm{Bil}_{3}$. Given $K_{s p}=7.71 \times 10^{-19}$, we have

$$
\begin{gathered}
K_{s p}=7.71 \times 10^{-19}=\left[\mathrm{Bi}^{3+}\right]\left[\mathrm{I}^{-}\right]^{3}=(S) \times(3 S)^{3}=27 S^{4} \\
\therefore S=\left(\frac{7.71 \times 10^{-19}}{27}\right)^{1 / 4}=1.30 \times 10^{-5} \mathrm{M}
\end{gathered}
$$

- The correct answer is $\mathbf{B}$.

Part 7: Assuming that NaCl dissociates completely, the initial concentration of $\mathrm{Cl}^{-}$ion in the solution will be 0.20 M . We proceed to draw up the following concentration diagram.

| Conc. | $\mathrm{AgCl}(\mathrm{s})$ | $\mathrm{Ag}^{+}$ | $\mathrm{Cl}^{-}$ |
| :---: | :---: | :---: | :---: |
| Initial | - | 0 | 0.20 |
| Change | - | $+S$ | $+S$ |
| Final | - | $S$ | $S+0.20$ |

Then, in view of $K_{s p}=1.6 \times 10^{-10}$, we have

$$
K_{s p}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right] \rightarrow 1.6 \times 10^{-10}=S \times(S+0.20)
$$

Since $S$ is most likely much lower than 0.20 , we simplify to give

$$
\begin{gathered}
1.6 \times 10^{-10}=S \times(S+0.20) \approx 0.2 S \\
\therefore S=8.0 \times 10^{-10} \mathrm{M}
\end{gathered}
$$

The solubility of AgCl in a solution containing $0.20 \mathrm{M} \mathrm{NaCl}(\mathrm{aq})$ is $8.0 \times 10^{-10}$ M.

- The correct answer is $\mathbf{A}$.

Part 8: Assuming that $\mathrm{FeCl}_{2}$ dissociates completely, the initial concentration of $\mathrm{Fe}^{2+}$ ion in the solution will be $2.5 \times 10^{-3} \mathrm{M}$. Accordingly, we prepare the following concentration diagram.

| Conc. | $\mathrm{Fe}(\mathrm{OH})_{2}(\mathrm{~s})$ | $\mathrm{Fe}^{2+}$ | $\mathrm{OH}^{-}$ |
| :---: | :---: | :---: | :---: |
| Initial | - | $2.5 \times 10^{-3}$ | 0 |
| Change | - | $+S$ | $+2 S$ |
| Final | - | $2.5 \times 10^{-3}+S$ | $2 S$ |

Then, knowing that $K_{s p}=1.6 \times 10^{-14}$, we have

$$
K_{s p}=\left[\mathrm{Fe}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2} \rightarrow 1.6 \times 10^{-14}=\left(2.5 \times 10^{-3}+S\right) \times(2 S)^{2}
$$

Assuming $S$ is negligible in $2.5 \times 10^{-3}+S$, we can simplify and obtain

$$
\begin{gathered}
1.6 \times 10^{-14}=\left(2.5 \times 10^{-3}+S\right) \times(2 S)^{2} \approx 2.5 \times 10^{-3} \times 4 S^{2} \\
\therefore 1.6 \times 10^{-14}=10^{-2} S^{2} \\
\therefore S=\left(\frac{1.6 \times 10^{-14}}{10^{-2}}\right)^{1 / 2}=1.26 \times 10^{-6} \mathrm{M}
\end{gathered}
$$

The solubility of $\mathrm{Fe}(\mathrm{OH})_{2}$ in a solution containing $2.5 \mathrm{mM} \mathrm{FeCl} 2(\mathrm{aq})$ is $1.26 \times 10^{-6} \mathrm{M}$.

- The correct answer is $\mathbf{B}$.

Part 9: Assuming that NaCl dissociates completely, the initial concentration of $\mathrm{Cl}^{-}$ion in the solution will be 0.15 M . Therefore, we can propose the following concentration diagram.

| Conc. | $\mathrm{Hg}_{2} \mathrm{Cl}_{2}(\mathrm{~s})$ | $\mathrm{Hg}_{2}{ }^{2+}$ | $\mathrm{Cl}^{-}$ |
| :---: | :---: | :---: | :---: |
| Initial | - | 0 | 0.15 |
| Change | - | $+S$ | $+2 S$ |
| Final | - | $S$ | $0.15+2 S$ |

Since $K_{s p}=2.6 \times 10^{-18}$, it follows that

$$
K_{s p}=\left[\mathrm{Hg}_{2}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{2} \rightarrow 2.6 \times 10^{-18}=S \times(0.15+2 S)^{2}
$$

With the assumption that $S$ is negligible in $0.15+2 S$, we can simplify and obtain

$$
\begin{gathered}
\therefore 2.6 \times 10^{-18}=S \times(0.15+2 S)^{2} \approx 0.15^{2} \times S \\
\therefore S=\frac{2.6 \times 10^{-18}}{0.15^{2}}=1.16 \times 10^{-16} \mathrm{M}
\end{gathered}
$$

The solubility of $\mathrm{Hg}_{2} \mathrm{Cl}_{2}$ in a solution containing $0.15 \mathrm{M} \mathrm{Hg}_{2} \mathrm{Cl}_{2}(\mathrm{aq})$ is $1.16 \times 10^{-16} \mathrm{M}$.

- The correct answer is $\mathbf{A}$.

Part 10: The solubility $S_{1}$ of salt MX is given by

$$
\begin{gathered}
{\left[\mathrm{M}^{+}\right]\left[\mathrm{X}^{-}\right]=K_{s p} \rightarrow S_{1} \times S_{1}=4.0 \times 10^{-8}} \\
\therefore S_{1}^{2}=4.0 \times 10^{-8}
\end{gathered}
$$

$$
\therefore S_{1}=\sqrt{4.0 \times 10^{-8}}=2.0 \times 10^{-4} \mathrm{M}
$$

The solubility $S_{2}$ of salt $\mathrm{MX}_{2}$ is, in turn,

$$
\begin{gathered}
{\left[\mathrm{M}^{2+}\right]\left[\mathrm{X}^{-}\right]^{2}=K_{s p} \rightarrow S_{2} \times\left(2 S_{2}\right)^{2}=3.2 \times 10^{-14}} \\
\therefore 4 S_{2}^{3}=3.2 \times 10^{-14} \\
\therefore S_{2}=\left(\frac{3.2 \times 10^{-14}}{4}\right)^{1 / 3}=2.0 \times 10^{-5} \mathrm{M}
\end{gathered}
$$

The solubility $S_{3}$ of salt $M_{3} X$ is, in sequence,

$$
\begin{gathered}
{\left[\mathrm{M}^{+}\right]^{3}\left[\mathrm{X}^{3-}\right]=K_{s p} \rightarrow\left(3 S_{3}\right)^{3} \times S_{3}=2.7 \times 10^{-15}} \\
\therefore 27 S_{3}^{4}=2.7 \times 10^{-15} \\
\therefore S_{3}=\left(\frac{2.7 \times 10^{-15}}{27}\right)^{1 / 4}=1.0 \times 10^{-4}
\end{gathered}
$$

Accordingly, the correct order of solubilities is $M X>M_{3} X>M X_{2}$.

- The correct answer is D.


## P. $9 \rightarrow$ Solution

Part 1: The molarity at which salt begins to precipitate is found from the solubility product of AgCl , namely,

$$
\begin{aligned}
& K_{s p}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right] \rightarrow\left[\mathrm{Ag}^{+}\right]=\frac{K_{s p}}{\left[\mathrm{Cl}^{-}\right]} \\
& \therefore\left[\mathrm{Ag}^{+}\right]=\frac{1.6 \times 10^{-10}}{1.0 \times 10^{-5}}=1.6 \times 10^{-5} \mathrm{M}
\end{aligned}
$$

Given the molar weight of silver nitrate $=170 \mathrm{~g} / \mathrm{mol}$, the mass of salt required for the onset of precipitation is calculated as

$$
m=\frac{1.6 \times 10^{-5} \mathrm{~mol}}{1 \mathrm{~L}} \times \frac{170 \mathrm{~g}}{\mathrm{~mol}} \times 0.1 \mathrm{~L} \times \frac{10^{6} \mu \mathrm{~g}}{\mathrm{~g}}=272 \mu \mathrm{~g} \mathrm{AgNO}_{3}
$$

- The correct answer is C.

Part 2: Given the solubility product $K_{s p}=6.5 \times 10^{-18}$, the concentration of hydroxyl ions at which precipitation begins is calculated as

$$
\begin{gathered}
K_{s p}=\left[\mathrm{Ni}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2} \rightarrow\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{K_{s p}}{\left[\mathrm{Ni}^{2+}\right]}} \\
\therefore\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{6.5 \times 10^{-18}}{0.05}}=1.14 \times 10^{-8} \mathrm{M}
\end{gathered}
$$

This corresponds to a $\mathrm{pOH}=-\log \left(1.14 \times 10^{-8}\right)=7.94$ and a pH such that

$$
p \mathrm{H}=14-p \mathrm{OH}=14-7.94=6.06
$$

Precipitation of nickel hydroxide commences in a mildly acidic environment.

- The correct answer is A.

Part 3: The pertinent equilibrium when NaCl is added to the silver nitrate solution is

$$
\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \rightleftarrows \mathrm{AgCl}(\mathrm{~s}) ; K_{s p}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]=1.6 \times 10^{-10}
$$

One drop contains $1 / 20=0.05 \mathrm{~mL}=0.05 \times 10^{-3}=5 \times 10^{-5} \mathrm{~L}$, and, given the concentration of NaCl solution $=0.01 \mathrm{M}$, corresponds to $5 \times 10^{-5} \times 0.01=$ $5 \times 10^{-7} \mathrm{~mol}$ chloride ions. In turn, the amount of silver ions in 10 mL of 0.004 M $\mathrm{AgNO}_{3}$ solution is $0.01 \times 0.004=4 \times 10^{-5} \mathrm{~mol}$. Neglecting the volume of the NaCl solution drop, the solubility quotient shoukl be

$$
Q_{s p}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]=\left(\frac{4 \times 10^{-5}}{0.01}\right) \times\left(\frac{5 \times 10^{-7}}{0.01}\right)=2.0 \times 10^{-7}
$$

Since $Q_{s p}>K_{s p}(\mathrm{AgCl})=1.6 \times 10^{-10}$, a precipitate will form. Now, the pertaining equilibrium when NaCl is added to the lead chloride solution is

$$
\mathrm{Pb}^{2+}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq}) \rightleftarrows \mathrm{PbCl}_{2}(\mathrm{~s}) ; K_{s p}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{2}=1.7 \times 10^{-5}
$$

The amount of lead ions in 10 mL of $0.004 \mathrm{M} \mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ solution is $0.01 \times$ $0.004=4 \times 10^{-5} \mathrm{~mol}$. Neglecting the volume of the NaCl solution drop as before, the value of $Q_{s p}$ is

$$
Q_{s p}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{2}=\left(\frac{4 \times 10^{-5}}{0.01}\right) \times\left(\frac{5 \times 10^{-7}}{0.01}\right)^{2}=1.0 \times 10^{-11}
$$

Since $Q_{s p}<K_{s p}\left(\mathrm{PbCl}_{2}\right)=1.7 \times 10^{-5}$, a precipitate will not form.

- The correct answer is B.

Part 4: The order of solubility products is $K_{s p}\left[\mathrm{Ni}(\mathrm{OH})_{2}\right]<K_{s p}\left[\mathrm{Mg}(\mathrm{OH})_{2}\right]<$ $K_{s p}\left[\mathrm{Ca}(\mathrm{OH})_{2}\right]$. Accordingly, the order with which the compounds will precipitate, first to last, is $\mathrm{Ni}(\mathrm{OH})_{2}, \mathrm{Mg}(\mathrm{OH})_{2}, \mathrm{Ca}(\mathrm{OH})_{2}$.

## - The correct answer is $\mathbf{C}$.

Part 5: Given the solubility product of calcium hydroxide, $K_{s p}=5.5 \times 10^{-6}$, the concentration of hydroxyl ions at which calcium hydroxide begins to precipitate is found as

$$
\begin{gathered}
K_{s p}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}=5.5 \times 10^{-6} \rightarrow\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{5.5 \times 10^{-6}}{\left[\mathrm{Ca}^{2+}\right]}} \\
\therefore\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{5.5 \times 10^{-6}}{0.001}}=0.0742 \mathrm{M}
\end{gathered}
$$

This corresponds to a $p \mathrm{HH}=-\log (0.0742)=1.13$, and a $p \mathrm{H}=14-1.13=$ 12.87.

In view of the solubility product of magnesium hydroxide, $K_{s p}=1.1 \times 10^{-11}$, the concentration of $\mathrm{OH}^{-}$ions at which the compound begins to precipitate is calculated as

$$
\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{K_{s p}}{\left[\mathrm{Mg}^{2+}\right]}}=\sqrt{\frac{1.1 \times 10^{-11}}{0.001}}=1.05 \times 10^{-4} \mathrm{M}
$$

This corresponds to a $p \mathrm{OH}=-\log \left(1.05 \times 10^{-4}\right)=3.98$, and a $p \mathrm{H}=14$ $3.98=10.0$.

Knowing the solubility product of nickel(II) hydroxide, $K_{s p}=6.5 \times 10^{-18}$, the concentration of $\mathrm{OH}^{-}$ions at which the compound begins to precipitate is computed as

$$
\left[\mathrm{OH}^{-}\right]=\sqrt{\frac{K_{s p}}{\left[\mathrm{Ni}^{2+}\right]}}=\sqrt{\frac{6.5 \times 10^{-18}}{0.001}}=8.06 \times 10^{-8} \mathrm{M}
$$

This corresponds to a $p \mathrm{OH}=-\log \left(8.06 \times 10^{-8}\right)=7.09$, and a $p \mathrm{H}=14$ $7.09=6.91$.

ANSWER SUMMARY

| Problem 1 | 1.1 | B |
| :---: | :---: | :---: |
|  | 1.2 | C |
| Problem 2 | 2.1 | $\alpha$ |
|  | 2.2 | T/F |
|  | 2.3 | B |
| Problem 3 | 3.1 | $\alpha$ |
|  | 3.2 | C |
|  | $3 \cdot 3$ | B |
|  | $3 \cdot 4$ | A |
|  | $3 \cdot 5$ | B |
|  | 3.6 | A |
|  | 3.7 | B |
|  | 3.8 | C |
|  | $3 \cdot 9$ | D |
|  | 3.10 | C |
|  | 3.11 | D |
| Problem 4 | 4.1 | C |
|  | 4.2 | A |
|  | $4 \cdot 3$ | C |
|  | $4 \cdot 4$ | D |
| Problem 5 | 5.1 | A |
|  | 5.2 | T/F |
| Problem 6 | 6.1 | C |
|  | 6.2 | D |
|  | 6.3 | C |
|  | 6.4 | A |
|  | 6.5 | D |
|  | 6.6 | C |
|  | 6.7 | D |
|  | 6.8 | A |
|  | 6.9 | B |
| Problem 7 | 7.1 | B |
|  | 7.2 | B |
| Problem 8 | 8.1 | A |
|  | 8.2 | C |
|  | 8.3 | B |
|  | 8.4 | D |
|  | 8.5 | D |
|  | 8.6 | B |
|  | 8.7 | A |
|  | 8.8 | B |
|  | 8.9 | A |
|  | 8.10 | D |
| Problem 9 | 9.1 | C |
|  | 9.2 | A |
|  | 9.3 | B |
|  | 9.4 | C |
|  | $9 \cdot 5$ | Open-ended pb. |

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