

HINTS & SOLUTIONS WORKBOOK - 2

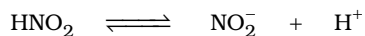
Ionic Equilibrium

Daily Tutorial Sheet

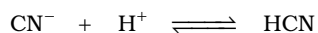
Level-0

Very Short Answer Type (1 Mark)

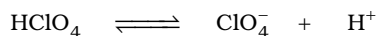
1. An acid – base pair which differ by a proton (H^+) is known as conjugate acid – base pair.



Acid Conjugate base



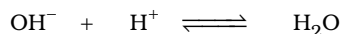
Base Conjugate acid



Acid Conjugate base



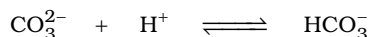
Base Conjugate acid



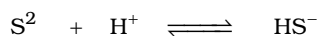
Base Conjugate acid



Acid Conjugate base



Base Conjugate acid



Base Conjugate acid

2. BF_3, H^+ and NH_4^+ act as Lewis acids as they have a vacant orbital and can take up an electron pair.

3. $HF \rightleftharpoons F^- + H^+$; $H_2SO_4 \rightleftharpoons HSO_4^- + H^+$; $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$

F^-, HSO_4^-, CO_3^{2-} = conjugate base

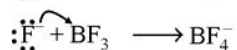
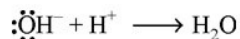
4. $NH_2^- + H^+ \rightleftharpoons NH_3$; $NH_3 + H^+ \rightleftharpoons NH_4^+$; $HCOO^- + H^+ \rightleftharpoons HCOOH$

$NH_3, NH_4^+, HCOOH$ = conjugate acid

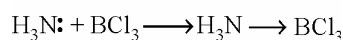
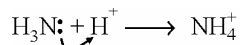
5.

| Species | Conjugate acid | Conjugate base |
|-----------|----------------|----------------|
| H_2O | H_3O^+ | OH^- |
| HCO_3^- | H_2CO_3 | CO_3^{2-} |
| HSO_4^- | H_2SO_4 | SO_4^{2-} |
| NH_3 | NH_4^+ | NH_2^- |

6. OH^- and F^- are electron rich species and can donate electron pair. Hence, these act as Lewis base.



H^+ and BCl_3 are electron deficient species and can accept electron pair. Hence, these can act as Lewis acid.



Short Answer Type-I (2 Marks)

7. If K_a is the ionization constant of a weak acid (HA) and K_{cb} is the ionization constant of its conjugate base (A^-) then $K_a \cdot K_{cb} = K_w$

$$K_b(\text{F}^-) = \frac{1 \times 10^{-14}}{K_a(\text{HF})} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} = 147 \times 10^{-11}$$

$$K_b(\text{HCOO}^-) = \frac{1 \times 10^{-14}}{K_a(\text{HCOOH})} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$$K_b(\text{CN}^-) = \frac{1 \times 10^{-14}}{K_a(\text{HCN})} = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

8. (i) $\text{H}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HS}^-$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

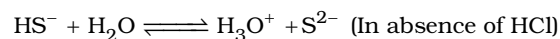
$$\Rightarrow [\text{H}_3\text{O}^+] = [\text{HS}^-] = \sqrt{K_{a_1} \cdot C} = \sqrt{9.1 \times 10^{-8} \times 0.1} = 9.54 \times 10^{-5} \text{ M}$$

- (ii) In the presence of 0.1 M HCl, $[\text{H}_3\text{O}^+] = 0.1 \text{ M}$

$$K_{a_1} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \Rightarrow 9.1 \times 10^{-8} = \frac{[0.1][\text{HS}^-]}{[0.1]} \Rightarrow [\text{HS}^-] = 9.1 \times 10^{-8} \text{ M}$$

Hence, concentration of $[\text{HS}^-]$ is decreased in the presence of 0.1 M HCl due to common-ion effect.

- (iii) For second dissociation constant,



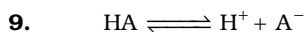
$$[\text{HS}^-] = 9.54 \times 10^{-5} \text{ M} \quad ; \quad K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

$$[\text{H}_3\text{O}^+] = [\text{S}^{2-}] = \sqrt{K_{a_2} \cdot C} = \sqrt{1.2 \times 10^{-13} \times 9.54 \times 10^{-5}} = 3.38 \times 10^{-9} \text{ M}$$

- (iv) In the presence of 0.1 M HCl,

$$K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]} = 1.2 \times 10^{-13} = \frac{[0.1][\text{S}^{2-}]}{[9.1 \times 10^{-8}]}$$

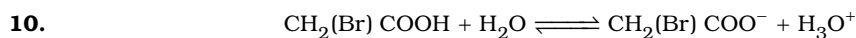
$$\Rightarrow [\text{S}^{2-}] = 1.092 \times 10^{-19} \text{ M}$$



$$\text{pH} = 4.15 = -\log(\text{H}^+) \Rightarrow [\text{H}^+] = [\text{A}^-] = 7.079 \times 10^{-5} \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(7.079 \times 10^{-5})(7.079 \times 10^{-5})}{0.01} = 5.0 \times 10^{-7}$$

$$\text{p}K_a = -\log K_a = -\log[5.0 \times 10^{-7}] = 7 - 0.699 = 6.301$$

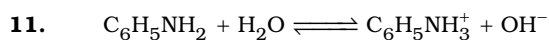


| | | | |
|---------------|---------------|-----------|-----------|
| Initial conc. | C | 0 | 0 |
| Equil. Conc. | $C - C\alpha$ | $C\alpha$ | $C\alpha$ |

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \Rightarrow K_a = C\alpha^2 \quad [\text{For weak acid } (1-\alpha) \approx 1]$$

$$K_a = 0.1 \times (0.132)^2 = 0.00174 \approx 1.74 \times 10^{-3}$$

$$\text{pH} = -\log \sqrt{K_a C} = -\log \sqrt{1.74 \times 10^{-3} \times 0.1} = 1.88 \quad [[\text{H}^+] = C\alpha = \sqrt{K_a \times C}]$$



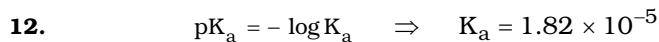
$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]} = \frac{[\text{OH}^-]^2}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

$$[\text{OH}^-] = \sqrt{K_b \cdot C} = \sqrt{4.27 \times 10^{-10} \times 0.001} = 6.534 \times 10^{-7}$$

$$\text{pOH} = -\log [6.534 \times 10^{-7}] = 7 + (-0.8152) = 6.18$$

For Base and Conjugate acid pair we have : $\text{pH} + \text{pOH} = 14$

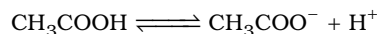
or $\text{pH of conjugate acid} = 14 - 6.18 = 7.82$



$$\alpha = \sqrt{K_a / C} \text{ or } \alpha = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} \quad (C = 0.05 \text{ given})$$

$$\alpha = \sqrt{\frac{1.82 \times 10^{-5}}{5.0 \times 10^{-2}}} = \sqrt{0.364 \times 10^{-3}} = \sqrt{3.64 \times 10^{-4}} \Rightarrow \alpha = 1.908 \times 10^{-2}$$

(a) In the presence of 0.01 M H^+



| | | | |
|----------------|------------------|----------------|--------------------|
| Initial conc. | 0.05 M | 0 | 0 |
| Equilib. conc. | $0.05 - C\alpha$ | $C\alpha$ | $(C\alpha + 0.01)$ |
| | ≈ 0.05 | ≈ 0.01 | |

$[\text{CH}_3\text{COOH}]$ is a weak acid and HCl is a strong acid, so we can assume that $(C\alpha + 0.01) \approx 0.01$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \Rightarrow 1.82 \times 10^{-5} = \frac{C\alpha \times 0.01}{0.05} \Rightarrow \alpha = 1.82 \times 10^{-3}$$

(b) In the presence of 0.1 M HCl: similarly, $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$

$$1.82 \times 10^{-5} = \frac{C\alpha \times 0.1}{0.05} \quad \left[[\text{H}^+] = (C\alpha + 0.1) \approx 0.1 \text{ M} \right]$$

$$\Rightarrow \alpha = \frac{0.91 \times 10^{-5}}{0.05} = 1.82 \times 10^{-4}$$

Note : In the presence of strong acid, dissociation of weak acid i.e., CH_3COOH decreases due to common ion effect. Also observe that we neglect the contribution of common ion from the weak electrolyte in such cases.

Short Answer Type-II (3 Marks)

13. Given, K_b for dimethylamine = 5.4×10^{-4} ; C for dimethylamine = 0.02 M

$$\alpha = \sqrt{K_b / C} = \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} = 1.64 \times 10^{-1} = 0.164$$

| | | | |
|---------------------------------|---|-----------|-----------------|
| In the presence of 0.1 M NaOH : | $(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$ | | |
| Initial conc. | 0.02M | 0 | 0 |
| Equilibrium conc. | $(0.02 - C\alpha)$ | $C\alpha$ | $C\alpha + 0.1$ |
| | ≈ 0.02 | | ≈ 0.1 |

(0.1 M OH^- from 0.1 M NaOH)

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} \Rightarrow 5.4 \times 10^{-4} = \frac{C\alpha \times 0.1}{0.02} \Rightarrow \alpha = 0.54 \%$$

14. $\text{pH} = -\log_{10} [\text{H}^+] \Rightarrow [\text{H}^+] = 10^{-\text{pH}}$

(a) pH of human muscle fluid = 6.83 $\Rightarrow [\text{H}^+] = 1.479 \times 10^{-4} \text{ M}$

(b) pH of human stomach fluid = 1 $\Rightarrow [\text{H}^+] = 6.31 \times 10^{-2} \text{ M}$

(c) pH of human blood = 7.38 $\Rightarrow [\text{H}^+] = 4.169 \times 10^{-8} \text{ M}$

(d) pH of human saliva = 6.4 $\Rightarrow [\text{H}^+] = 3.981 \times 10^{-7} \text{ M}$

Note : The idea behind this question was to remember the pH of given species (fluids).

15. (a) pH of milk = 6.8 $\Rightarrow [\text{H}^+] = 1.585 \times 10^{-7} \text{ M}$

(b) pH of black coffee = 5.0 $\Rightarrow [\text{H}^+] = 10^{-5} \text{ M}$

(c) pH of lemon juice = 2.2 $\Rightarrow [\text{H}^+] = 6.310 \times 10^{-3} \text{ M}$

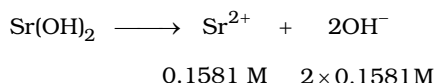
(d) pH of tomato juice = 4.2 $\Rightarrow [\text{H}^+] = 6.310 \times 10^{-5} \text{ M}$

(e) pH of egg white = 7.8 $\Rightarrow [\text{H}^+] = 1.585 \times 10^{-8} \text{ M}$

Note : The idea behind this question was also to remember the pH of given species (Liquids).

16. Solubility of $\text{Sr}(\text{OH})_2$ = 19.23 g/L at 298 K.

$$\text{Solubility in mol/L : } M = \frac{19.23}{121.6 \text{ g mol}^{-1}}$$

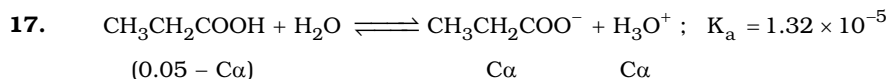


$$\Rightarrow [\text{Sr}^{2+}] = 0.1581 \text{ M} \quad \text{and} \quad [\text{OH}^-] = 0.3163 \text{ M}$$

In an aqueous solution at 25°C :

$$[\text{H}^+][\text{OH}^-] = K_w = 10^{-14} \Rightarrow [\text{H}^+] = \frac{10^{-14}}{0.3162} = 3.16 \times 10^{-14}$$

$$\Rightarrow \text{pH} = 14.04997 = 13.5003 \approx 13.5$$



From Ostwald's dilution law : $\alpha = \sqrt{K_a / C} = \sqrt{\frac{1.32 \times 10^{-5}}{0.05}} \Rightarrow \alpha = 0.016248$

$$[\text{H}_3\text{O}^+] = C\alpha = 0.05 \times 0.016248 = 8.124 \times 10^{-4} \Rightarrow \text{pH} \approx 3.09$$

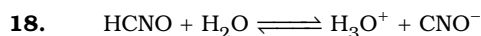
When the solution contains 0.01 M HCl : $K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}_3\text{O}^+]}{\text{CH}_3\text{CH}_2\text{COOH}}$

$$1.32 \times 10^{-5} = \frac{C\alpha \times 0.01}{(0.05 - C\alpha)} \approx \frac{C\alpha \times 0.01}{0.05}$$

$$[\text{H}_3\text{O}^+] = 0.01 \text{ M from HCl, } C = 0.01 \text{ M}$$

(In the presence of 0.01 M HCl dissociation of propanoic acid decreases, so degree of ionization is very less)

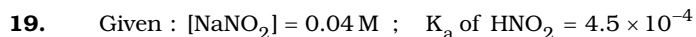
$$\text{Degree of ionization, } \alpha = 1.32 \times 10^{-3}$$



$$\text{pH} = 2.34 \Rightarrow [\text{H}^+] = [\text{H}_3\text{O}^+] = 4.57 \times 10^{-3} \text{ M}$$

$$\text{Degree of ionization, } \alpha = \frac{4.57 \times 10^{-3}}{0.1} = 4.57 \times 10^{-2}$$

$$\text{Ionization constant, } K_a = \frac{[\text{H}_3\text{O}^+][\text{CNO}^-]}{[\text{HCNO}]} = \frac{4.57 \times 10^{-3} \times 4.57 \times 10^{-3}}{0.1} = 2.089 \times 10^{-4}$$



Note that NaNO_2 is a salt of strong base, NaOH and weak acid, HNO_2 .

Using standard result for the pH of a solution of salt of Strong base and Weak acid:

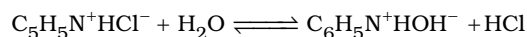
$$\text{pH} = 7 + \frac{\text{p}K_a + \log C}{2}$$

$$\text{p}K_a = 4 - 0.6532 = 3.3468 \approx 3.35 \Rightarrow \text{pH} = 7 + \frac{3.35 + \log 0.04}{2} = 7.98$$

$$\text{Degree of hydrolysis, } h = \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{10^{-14}}{4.5 \times 10^{-4} \times 0.04}} \Rightarrow h = 2.36 \times 10^{-5}$$

Long Answer Type (5 Marks)

20. The aqueous solution of pyridium hydrochloride is an acidic solution due to hydrolysis. Observe that it is a salt of strong acid, HCl and weak base, Pyridine.



Using standard result of pH :

$$\text{pH} = 7 - \frac{\text{pK}_b}{2} - \frac{\log C}{2} \Rightarrow 3.44 = 7 - \frac{\text{pK}_b}{2} - \frac{\log 0.02}{2}$$

On solving and substituting values, $\text{K}_b = 1.5 \times 10^{-9}$

21.

| | Salt | Acid | Base | Hydrolysis reaction | Nature of solution |
|-------|--------------------------|----------------|------------------------|---|--------------------|
| (i) | NaCl | HCl | NaOH | $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ No hydrolysis | Neutral |
| (ii) | KBr | HBr | KOH | No hydrolysis | Neutral |
| (iii) | NaCN | HCN | NaOH | $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$ | Basic |
| (iv) | NH_4NO_3 | HNO_2 | NH_4OH | $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$ | Acid |
| (v) | NaNO_2 | HNO_2 | NaOH | $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$ | Basic |
| (vi) | KF | HF | KOH | $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$ | Basic |

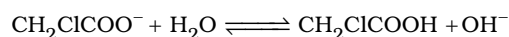
22. $\text{CH}_2\text{ClCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{ClCOO}^- + \text{H}_3\text{O}^+ ; \quad \text{K}_a = 1.35 \times 10^{-3}$

(a) $\text{pK}_a = -\log \text{K}_a = -\log [1.35 \times 10^{-3}] = 2.87$

By Oswald's dilution law : $[\text{H}_3\text{O}^+] = \sqrt{\text{K}_a \cdot C} = \sqrt{1.35 \times 10^{-3} \times 0.1} = 1.16 \times 10^{-2} \text{ M}$

$\text{pH acid} = -\log [\text{H}_3\text{O}^+] = -\log (1.16 \times 10^{-2}) \text{ M} = 1.94$

- (b) A 0.1 M $\text{CH}_2\text{ClCOONa}$ aqueous solution (sodium chloro-acetate) is basic due to hydrolysis.



Using standard result for pH of a salt of strong base and weak acid:

$$\text{pH} = 7 + \frac{\text{pK}_a + \log C}{2} = 7 + \frac{2.87 + \log 0.1}{2} = 7.94$$

23. (a) meq of $\text{Ca}(\text{OH})_2 = 2 \times 0.2 \times 10 = 4$

meq of HCl = $1.01 \times 25 = 2.5 \Rightarrow$ Solution is basic.

Excess meq of base = 1.5

$$\Rightarrow [\text{OH}^-] = \frac{1.5}{35} = 0.043 \text{ M} \Rightarrow \text{pH} = 14 + \log [\text{OH}^-] = 12.63$$

Note : Molarity of OH^- ions = Normality of OH^- ions as n-factor of OH^- ions is 1.

- (b) Observe clearly that :

meq of $\text{H}_2\text{SO}_4 = \text{meq of Ca}(\text{OH})_2$

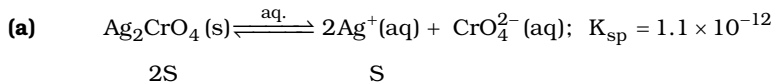
So it is neutral solution as salt is of strong Acid and Strong base. $\text{pH} = 7$

- (c) meq of acid = $2 \times 0.1 \times 10 = 2$
meq of base = $1 \times 0.1 \times 10 = 1 \Rightarrow$ Solution is acid.

$$[\text{H}^+]_{\text{excess}} = \frac{1}{20} \Rightarrow \text{pH} = -\log \frac{1}{20} = 1.3$$

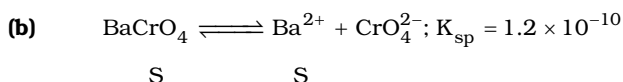
Note that molarity of H^+ ions is same as its normally as n-factor of H^+ ion is 1.

24. Let 's' be the solubility of each salt in mol/L.



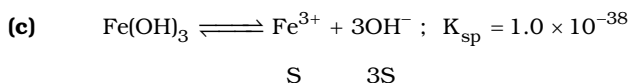
$$K_{\text{sp}} = [\text{Ag}^+]^2 \cdot [\text{CrO}_4^{2-}] = [2\text{S}]^2 \cdot [\text{S}] = 4\text{S}^3 \Rightarrow \text{S}^3 = \frac{K_{\text{sp}}}{4} \Rightarrow \text{S} \approx 6.5 \times 10^{-5} \text{ M}$$

$$\Rightarrow [\text{CrO}_4^{2-}] = \text{S} = 6.5 \times 10^{-5} \text{ M} \text{ \& } [\text{Ag}^+] = 2\text{S} = 1.3 \times 10^{-4} \text{ M}$$



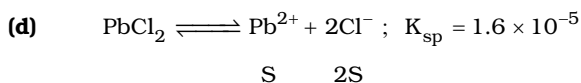
$$K_{\text{sp}} = [\text{Ba}^{2+}] \cdot [\text{CrO}_4^{2-}] = \text{S}^2 = 1.2 \times 10^{-10} \Rightarrow \text{S} = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5} \text{ M}$$

$$\Rightarrow [\text{Ba}^{2+}] = [\text{CrO}_4^{2-}] = 1.1 \times 10^{-5} \text{ M}$$



$$K_{\text{sp}} = [\text{Fe}^{3+}] [\text{OH}^-]^3 = \text{S} \cdot (3\text{S})^3 = 27\text{S}^4 \Rightarrow \text{S}^4 = \frac{K_{\text{sp}}}{27} \Rightarrow \text{S} \approx 1.39 \times 10^{-10}$$

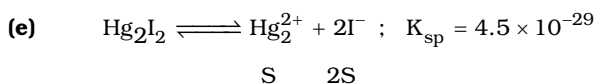
$$\Rightarrow [\text{Fe}^{3+}] = 1.39 \times 10^{-10} \text{ M} \text{ \& } [\text{OH}^-] = 3\text{S} = 3 \times 1.39 \times 10^{-10} = 4.17 \times 10^{-10} \text{ M}$$



$$K_{\text{sp}} = [\text{Pb}^{2+}] [\text{Cl}^-]^2 = \text{S} \cdot (2\text{S})^2 = 4\text{S}^3 \Rightarrow \text{S}^3 = \frac{K_{\text{sp}}}{4} \Rightarrow \text{S} \approx 1.59 \times 10^{-2} \text{ M}$$

$$\therefore \text{Solubility of } \text{PbCl}_2 = 1.59 \times 10^{-2} \text{ M}$$

$$\Rightarrow [\text{Pb}^{2+}] = 1.59 \times 10^{-2} \text{ M} \text{ \& } [\text{Cl}^-] = 2 \times 1.59 \times 10^{-2} \text{ M} = 3.18 \times 10^{-2} \text{ M}$$

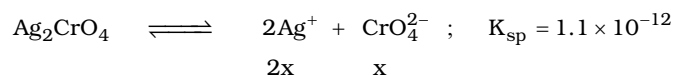


$$K_{\text{sp}} = [\text{Hg}_2^{2+}] [\text{I}^-]^2 = \text{S} \cdot (2\text{S})^2 = 4\text{S}^3 \Rightarrow \text{S}^3 = \frac{K_{\text{sp}}}{4} \Rightarrow \text{S} = 2.241 \times 10^{-10} \text{ M}$$

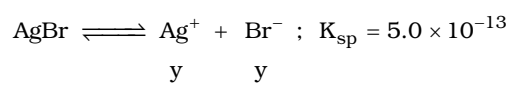
$$\text{Solubility of } \text{Hg}_2\text{I}_2 = 2.241 \times 10^{-10} \text{ M}$$

$$[\text{Hg}_2^{2+}] = 2.241 \times 10^{-10} \text{ M} \text{ \& } [\text{I}^-] = 2 \times 2.241 \times 10^{-10} \text{ M} = 4.482 \times 10^{-10} \text{ M}$$

25. Let x mol/L and y mol/L be the solubilities of Ag_2CrO_4 and AgBr respectively.



$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2\text{x})^2 \cdot \text{x} = 4\text{x}^3 \Rightarrow \text{x}^3 = \frac{K_{\text{sp}}}{4} \Rightarrow \text{x} = 6.503 \times 10^{-5} \text{ M}$$



$$K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = y \cdot y = y^2 \quad \Rightarrow \quad y = 7.07 \times 10^{-7} \text{ M}$$

$$\text{The ratio of solubilities} = \frac{x}{y} = \frac{6.5 \times 10^{-5}}{7.07 \times 10^{-7}} \approx 92$$