

## THE KEY

### ❑ CLASSIFICATION OF SUBSTANCES

On the basis of their dissociation nature :

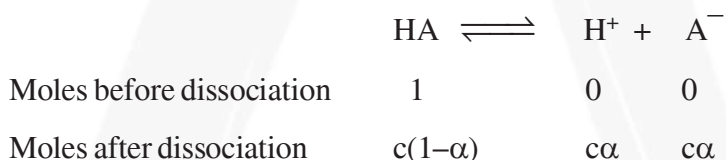
- (i) **Strong electrolytes** : Substances which are largely dissociated and are strong electrolytes. e.g. HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> etc.
- (ii) **Weak electrolytes** Substances which dissociate only to a small extent in aqueous solution. e.g. HCN, H<sub>3</sub>BO<sub>3</sub> etc.
- (iii) **Non electrolytes** Which do not dissociate.

**Note :** The above classification of substances in weak electrolyte and strong electrolyte is based on their dissociation nature in aqueous medium. However, such classification suffers a great drawback in the sense that a particular electrolyte, though strong in water, might behave as a weak one when dissolved in some other solvent or vice-versa. For example, sodium chloride acts as strong electrolyte in water but it acts as weak electrolyte in methanol. On the other hand, acetic acid a weak electrolyte in water acts as strong electrolyte in ammonia. NaCl is also strong electrolyte in ammonia.

### ❑ ARRHENIUS THEORY OF ELECTROLYTE DISSOCIATION

A chemical equilibrium exists between the undissociated electrolyte molecules and the ions that result from dissociation

Consider ionisation of a weak electrolyte say a monoprotic acid, acid HA



where,  $\alpha$  is degree of dissociation of weak acid HA. Let 'c' mole litre<sup>-1</sup> be concentration of acid HA, then

$$[\text{HA}] = c(1 - \alpha); \quad [\text{H}^+] = c\alpha; \quad [\text{A}^-] = c\alpha$$

According to equilibrium constant expression

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(c\alpha \cdot c\alpha)}{c(1 - \alpha)}$$

$$K_a = \frac{c\alpha^2}{(1 - \alpha)} \quad \dots(i)$$

where,  $K_a$  is dissociation constant of an acid.

### ❑ FACTORS INFLUENCING DEGREE OF DISSOCIATION

$$\alpha = \frac{\text{Moles dissociated at any time}}{\text{Total moles dissolved initially}}$$

- (1) Nature of solute
- (2) Nature of solvent
- (3) Temperature
- (4) Ostwald dilution law

Consider ionisation of a weak electrolyte say a monoprotic acid, acid HA



Moles before dissociation	1	0	0
Moles after dissociation	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(i)$$

where,  $K_a$  is dissociation constant of an acid. Since for weak electrolytes,  $\alpha$  is small and thus,  $1-\alpha \approx 1$

$$\therefore K_a = c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\left(\frac{K_a}{c}\right)} = \sqrt{K_a V} \quad \dots(ii)$$

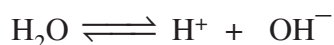
where,  $V$  is the volume in litre containing 1 mole of electrolyte. Thus it may be concluded that degree of dissociation of a weak electrolyte is inversely proportional to square root of its concentration.

(5)

The phenomenon in which degree of dissociation of a weak electrolyte is suppressed by the addition of a substance having an ion common to weak electrolyte is known as common ion effect.

### ❑ IONIC PRODUCT OF WATER

Pure water is weak electrolyte and dissociates as :

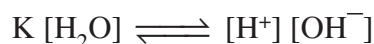


Before dissociation	1	0	0
After dissociation	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Applying law of mass action to dissociation equilibrium of water.

$$K_{eq} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

where,  $K_{eq}$  is dissociation constant or equilibrium constant of water. Since, dissociation of water is too less and thus,  $[H_2O]$ , i.e., undissociated  $H_2O$  can be taken as constant, therefore



$$K_w = [H^+] [OH^-]$$

The new constant  $K_w$  is known as ionic product of water. The numerical value of  $K_w$  increases considerably with temperature from  $0.11 \times 10^{-14}$  at  $0^\circ\text{C}$  to  $50 \times 10^{-14}$  at  $100^\circ\text{C}$ . It is  $1.0 \times 10^{-14}$  at  $25^\circ\text{C}$  which we will use frequently. The variation of ionic product of water with temperature is given by

$$2.303 \log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

### □ pH CONCEPT

Sorenson used a new term pH [small p, capital H, the H stands for hydrogen ion and the p for 'puissance' (French), 'potenz' (German) and power (English)] to express the hydrogen ion concentration.

$$\text{i.e.} \quad [H^+] = 10^{-\text{pH}}$$

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

$$\text{or} \quad \text{pH} = \log \frac{1}{[H^+]}$$

Alternatively pH is negative logarithm of magnitude of  $H^+$  concentration.

**Note :** The term pH comes from *pure voir hydrogene* which implies potential of hydrogen.

One should be very clear that no doubt pH is a measure of acidic nature but as pH goes up, the acidic nature goes down. Not only the relationship between pH and acidic nature is inverse but also a logarithmic one. A decrease of a single pH unit corresponds to a ten folds increase in acidic nature and when pH goes down by two units, acidic nature increases by a factor of 100.

Also hydrogen ion in a solution are not free floating portion of course. They are actually attached to molecules of solvent. For this reason  $H^+$  ions in water are often written as hydronium ions ( $H_3O^+$ ) and acidic nature is expressed in terms of ( $H_3O^+$ ). For simplicity hydrogen ions are simply written as  $H^+$ , with the understanding that  $H^+$ , ions in solution are always solvated.

Furthermore, Sorenson original definition of pH is still the one most widely used, but it is not complete satisfactory in all cases. As  $[H^+]$  increases, the effective concentration of  $H^+$  ions becomes progressively less than might be expected, because of increased inter ionic attractions at the higher concentrations. A more precise definition of pH is

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

Where,  $a_{H^+}$  is the hydrogen ion activity (or the effective  $H^+$  concentration). The  $H^+$  activity is obtained by multiplying  $[H^+]$  by a suitable activity coefficient based on thermodynamic measurements.

They approach 1.0 for very dilute solutions but get smaller as concentration increases.

It is therefore, clear that highly precise pH calculations require the use of activity coefficients but ordinarily pH is calculated from the simple relationship  $\text{pH} = -\log [\text{H}^+]$ , even though it tends to become less valid at higher concentrations.

### ❑ SALIENT FEATURES OF PH CONCEPT

- Theoretically pH values greater than 14 are possible for concentrated strong base and negative pH values are possible for concentrated strong acids, but it is for dilute solutions that pH scale is most useful. The pH for concentrated solution should be derived by  $\text{pH} = -\log a_{\text{H}^+}$  where  $a_{\text{H}^+}$  represents active mass of  $\text{H}^+$  ions.

- For any aqueous solution at  $25^\circ\text{C}$  it must be true that  $[\text{H}^+][\text{OH}^-] = 10^{-14}$

No matter how acidic or basic a solution might be, it must contain  $\text{H}^+$  and  $\text{OH}^-$  ions and the product of effective molar concentration equal to  $10^{-14}$  or  $K_w$

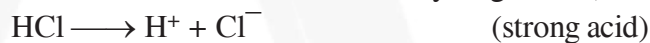
$$\begin{aligned}\text{Also} \quad & \log [\text{H}^+] + \log [\text{OH}^-] = 14 \\ \text{or} \quad & -\log [\text{H}^+] + (-\log [\text{OH}^-]) = 14 \\ \text{or} \quad & \text{pH} + \text{pOH} = 14\end{aligned}$$

### ❑ ACIDS AND BASES

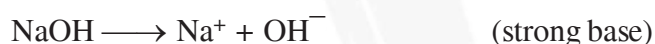
The initial classification of substances as acid was suggested by their sour taste (Latin acids-sour) and alkalies (alkali-ashes of a plant). Later on different nomenclature and classification of acids and base were given. Some important ones covering the present syllabus are given ahead.

### ❑ ARRHENIUS CONCEPT (1880-1890)

- An arrhenius acid is a substance which furnishes hydrogen ion ( $\text{H}^+$  ions) in aqueous solution, e.g.,



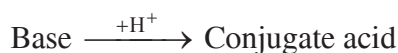
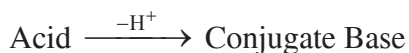
- An arrhenius base is a substance which furnishes hydroxyl ( $\text{OH}^-$ ) ions in aqueous solution, e.g.,



- The strength of an acid or base depends upon its tendency to furnish  $\text{H}^+$  or  $\text{OH}^-$  ions in solution respectively.

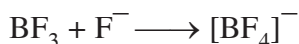
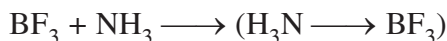
### ❑ BRONSTED-LOWRY CONCEPT (1923)

- A Bronsted acid is proton donor whereas, a Bronsted base is proton acceptor.
- A pair of Bronsted acid-base which differ by a proton is known as conjugate pair of Bronsted acid and Bronsted base.



### □ LEWIS CONCEPT (1923)

- (i) A Lewis acid is an electron pair acceptor. A Lewis base is an electron pair donor.



- (ii) **Simple cations:**  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{K}^+$  etc. are all Lewis acids.
- (iii) **Compounds whose central atom has incomplete octet :** All compounds having central atom with less than a full of electrons are Lewis acid, e.g.  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{RMgX}$ ,  $\text{MgCl}_2$  etc.
- (iv) **Lewis base :** Compounds having electron pair available for co-ordination show Lewis base nature, e.g.  $\text{:NH}_3$  etc.

### □ pH CALCULATION

#### Case (i) A weak acid in water

- (a) if  $\alpha = \sqrt{\frac{K_a}{C}}$  is  $< 0.1$ , then  $[\text{H}^+] \approx \sqrt{K_a C}$ .

- (b) **General Expression :**  $[\text{H}^+] = 0.5(-K_a + \sqrt{K_a^2 + 4K_a C})$

Similarly for a weak base, substitute  $[\text{OH}^-]$  and  $K_b$  instead of  $[\text{H}^+]$  and  $K_a$  respectively in these expressions.

#### Case (ii) A weak acid and a strong acid : Due to strong acid degree of dissociation of weak acid decreases.

#### Case (iii) Two (or more) weak acids

The accurate treatment yields a cubic equation. Assuming that acids dissociate to a negligible extent [ i.e.  $C - x \approx C$  ]  $[\text{H}^+] = (K_1 C_1 + K_2 C_2 + \dots + K_w)^{1/2}$

#### Case (iv) When dissociation of water becomes significant:

Dissociation of water contributes significantly to  $[\text{H}^+]$  or  $[\text{OH}^-]$  only when for

- (i) **Strong acids (or bases) :**

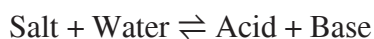
$10^{-8}\text{M} < C < 10^{-6}\text{M}$ . Neglecting ionisation of water at  $10^{-6}\text{M}$  causes 1% error (approvable). Below  $10^{-8}\text{M}$ , contribution of acid (or base) can be neglected and pH can be taken to be practically 7.

- (ii) **Weak acids (or bases) :** When  $K_a C < 10^{-12}$ , then consider dissociation of water as well.

#### Case (v) pH of solution involving a polyprotic acid or base depend upon $K_1$ , $K_2$ . Successive dissociation can be neglected.

### ❑ SALT HYDROLYSIS

The phenomenon of interaction of cations and anions of a salt with  $H_2O$  in order to produce acidic nature or alkaline nature is known as salt hydrolysis.

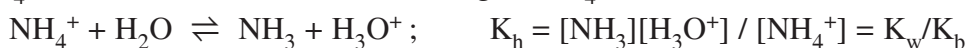


The process of salt hydrolysis is actually the reverse process of neutralization.

(i) **Salts of strong acids and strong bases** do not undergo hydrolysis.

(ii) **Salts of a strong acids and weak bases** give an acidic solution.

e.g.  $NH_4Cl$  when dissolved, it dissociates to give  $NH_4^+$  ions.



**Important !** In general :  $K_a$  (of an acid).  $K_b$  (of its conjugate base) =  $K_w$

If the degree of hydrolysis(h) is small ( $\ll 1$ ),  $h = \sqrt{K_h / C}$ .

$$pH = \frac{1}{2} (pk_w - pk_b - \log C)$$

$$\text{Otherwise } h = \frac{-K_h + \sqrt{K_h^2 + 4K_h C}}{2C}, \quad [H^+] = Ch$$

(iii) **Salts of strong base and weak acid** give a basic solution ( $pH > 7$ ) when dissolved in water, e.g.



$$[OH^-] = Ch, \quad h = \sqrt{K_h / C}$$

$$pH = \frac{1}{2} (pk_w + pk_a + \log C)$$

(iv) **Salts of weak base and weak acid**

Assuming degree of hydrolysis to be same for the both the ions,

$$K_h = K_w / (K_a \cdot K_b), \quad [H^+] = [K_a K_w / K_b]^{1/2}$$

$$pH = \frac{1}{2} (pk_w + pk_a - pk_b)$$

(v) **Amphiprotic salts**

e.g.  $NaHCO_3$

$$pH = \frac{1}{2} (pk_1 + pk_2)$$

**Note:** Exact treatment of case (iv) & (v) is difficult to solve. So use this assumption in general cases.

Also, degree of anion or cation will be much higher in the case of a salt of weak acid and weak base.

This is because each of them gets hydrolysed, producing  $H^+$  and  $OH^-$  ions. These ions combine to form water and the hydrolysis equilibrium is shifted in the forward direction.

### ❑ BUFFER SOLUTIONS

A solution whose pH does not change significantly on addition of a small amount of acid or alkali.

#### Type of Buffers

#### 1. Simple buffers

(i) A salt of weak acid and weak base in water e.g.  $CH_3COONH_4$ ,  $NH_4CN$

(ii) Proteins and amino acids



## 2. Mixed buffers

These are of two types :

## (i) Acidic buffer mixtures ; A weak acid with its conjugate base :

$\text{NaHCO}_3 + \text{H}_2\text{CO}_3$  ( $\text{H}_2\text{CO}_3$  ; is weak acid and  $\text{HCO}_3^-$  is its conjugate base ) ;

$\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  ;  $\text{NaH}_2\text{PO}_4 + \text{H}_3\text{PO}_4$ .

The pH of the buffer solution of this category not necessarily lie in between 0 to 7. It may be in the range of 7 to 14 depending upon the dissociation constant of acid.

**Henderson's Equation**

$\text{pH} = \text{pK}_a + \log \{[\text{salt}] / [\text{acid}]\}$  for weak acid with its conjugate base.

## (ii) Basic buffer mixtures ; A weak base with its conjugate Acid :

$\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$  (  $\text{NH}_4\text{OH}$  is weak base and  $\text{NH}_4^+$  is its conjugate acid.)

**Henderson's Equation**

$\text{pOH} = \text{pK}_b + \log \{[\text{salt}] / [\text{base}]\}$  for weak base with its conjugate acid.

**Important :** For good buffer capacity, [salt] : [acid] ratio should be as close to one as possible. In such a case,  $\text{pH} = \text{pK}_a$ . (This also is the case at midpoint of titration)

Buffer capacity = (no. of moles of acid (or base) added to 1L) / (change in pH)

□ **INDICATORS**

Indicator is a substance which indicates the point of equivalence in a titration by undergoing a change in its colour. They are weak acids or weak bases.

**Theory of Indicators.** The ionized and unionized forms of indicators have different colours. If 90 % or more of a particular form (ionised or unionised) is present, then its colour can be distinctly seen. In general, for an indicator which is weak acid,  $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$ , the ratio of ionized to unionized form can be determined from

$$\text{pH} = \text{pK}_a + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

So, for detectable colour change,  $\text{pH} = \text{pK}_a \pm 1$

This roughly gives the range of indicators. Ranges for some popular indicators are

**Table 1 : Indicators**

Indicators	pH range	Colour	
		acid medium	basic medium
Methyl Orange	3.1-4.4	pink	yellow
Methyl red	4.2-6.3	red	yellow
Litmus	5.5-7.5	red	blue
Phenol red	6.8-8.4	yellow	red
Phenolphthaleine	8.3-10	colourless	pink
Thymol blue	1.2-2.8	red	yellow

**Equivalence point.** The point at which exactly equivalent amounts of acid and base have been mixed.

**Acid Base Titration.** For choosing a suitable indicator titration curves are of great help. In a titration curve, change in pH is plotted against the volume of alkali to a given acid. Four cases arise.

- (a) **Strong acid vs strong base.** The curve is almost vertical over the pH range 3-10.
- (b) **Weak acid vs strong base.** The curve is almost vertical over the pH range 5-10. So, phenolphthalein is suitable.
- (c) **Weak base vs strong acid .** The curve is almost vertical over the pH range 9-3. Methyl red or methyl orange suitable.
- (d) **Weak acid vs weak base.** No sharp change in pH. No suitable indicator.

#### ❑ SOLUBILITY PRODUCT ( $K_{sp}$ ).

For sparingly soluble salts (eg.  $\text{Ag}_2\text{C}_2\text{O}_4$ ) an equilibrium which exists is



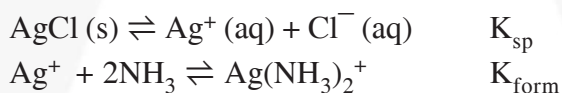
$$\text{Then } K_{sp} = [\text{Ag}^+]^2[\text{C}_2\text{O}_4^{2-}]$$

**Common ion effects.** Suppression of dissociation by adding an ion common with dissociation products. e.g.  $\text{Ag}^+$  or  $\text{C}_2\text{O}_4^{2-}$  in the above example.

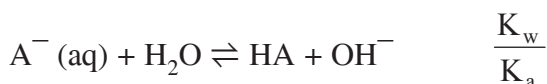
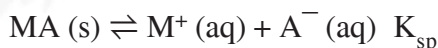


**Precipitation.** Whenever the product of concentrations (raised to appropriate power) exceeds the solubility product, precipitation occurs.

#### Effect of complex formation on solubility.



#### Effect of hydrolysis on solubility



$$S = \sqrt{K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_a} \right)}$$



## THE ATLAS

## Ionic Equilibrium

## The concept of ionic equilibria as equilibria involving ions in solution

- (i) Arrhenius theory of electrolytes.
- (ii) Ostwards dilution law for weak electrolyte  $K_a = \left(\frac{\alpha^2}{1-\alpha}\right)\left(\frac{1}{V}\right)$
- (iii) Acid & Bases
  - (a) Arrhenius  $H^+/OH^-$  theory.
  - (b) Bronsted lowery - protonic concept.
  - (c) Lewis concept - electronic concept of acids and bases.

## Some basic concept

- pH scale :  $pH = -\log[H^+]$ .
- (i) Water as amphotropic solvent.
  - (ii) Autoionization of water :  $K_w = [H^+][OH^-]$ .
  - (iii)  $K_a[H_2O] = K_w/[H_2O]$
  - (iv) Change in pH of neutral  $H_2O$  with temperature.

## Homogenons Ionic equilibria

- (i) Acid/ base equilibrium
  - (a) Strong acid  $[H^+] = c/2 + \sqrt{\frac{c^2}{4} + K_w}$ ;  $c = \text{conc. of (acid)}$
  - (b) pH due to polyprotic weak acids
  - (c) Weak monobasic acid  $[H^+] = \sqrt{K_a \cdot c}$  (if  $\alpha < 0.1$ )
  - (d) Mixture of S.A. & W.A.
  - (e) Mixture of two W.A.  $[H^+] = \sqrt{K_1 c_1 + K_2 c_2}$
  - (f) Buffer solutions :  $pH = pK_a + \log\left(\frac{\text{salt}}{\text{acid}}\right)$   
 $pOH = pK_b + \log\left(\frac{\text{salt}}{\text{base}}\right)$
  - (g) Salt hydrolysis – (W.A. & S.B)  $pH = \frac{1}{2}(pK_w + pK_a + \log c)$   
 (W.B & S.A.)  $pH = \frac{1}{2}(pK_w - pK_b - \log c)$   
 (W.A. & W.B.)  $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

## Heterogenons equilibria

- Solubility of sparingly soluble salt's  
 $(AB, AB_2, A_x B_y) K_{sp} = (S^{x+y}) X^x Y^y$
- (i) Effect of pH on solubility.
  - (ii) Simultaneous solubility.

## Application of both heterogenous and homogenous equilibrium

- (i) Extent of hydrolysis in buffer solution.
- (ii) Change in solubility due to complex formation.
- (iii) Solubility and hydrolysis.

BEWARE OF SNAKES

1. **General Mistake** : pH of a neutral water solution is always equal to 7.

**Explanation** : pH of neutral water depend on temperature. Since  $\text{pH (neutral point)} = \frac{\text{p}K_w}{2}$ ;  $\text{p}K_w$  decreases with temperature hence pH of neutral solution.

2. **General Mistake** : If a solution is diluted half times pH of solution becomes double.

**Explanation** : Infact pH increases by 0.3010 unit. If it is diluted x times pH increases by  $\log x$ .  
e.g. If solution is diluted 10 times pH increases by  $\log_{10} 10 = 1$  unit.

3. **General Mistake** : For calculation of pH of  $10^{-6}$  M  $\text{CH}_3\text{COOH}$  the formula  $(\text{H}^+) = \sqrt{K_a c}$  will give  $\text{pH} = -\log\left(\sqrt{1.8 \times 10^{-5} \times 10^{-6}}\right) = 5.37$ .

**Explanation** : 5.37 is incorrect answer. pH should be calculated by taking  $\alpha = \frac{-K_a + \sqrt{K_a^2 + 4K_a c}}{2c}$

4. **General Mistake** : If  $10^3$  mole  $\text{CH}_3\text{COONa}$  and 1 mole  $\text{CH}_3\text{COOH}$  is added in  $10^4$  litres water the pH of resulting solution is equal to  $\text{pH} = \text{p}K_a + \log \frac{10^3}{1} = 7.74$ .

**Explanation** : 7.74 is incorrect answer. The  $\text{CH}_3\text{COOH}$  concentration is too low to be taken as constituent of buffer solution. Use salt hydrolysis formula instead to calculate the pH.

5. **General Mistake** : The equilibrium concentration of anion and cation of a sparingly soluble salt ( $\text{A}_2\text{C}_3$ ) are a and c moles  $\text{lit}^{-1}$  respectively. The solubility product is  $(2a)^2 (3c)^3 = K_{sp}$

**Explanation** :  $K_{sp} = a^2 c^3$ .

6. **General Mistake** : pH of  $10^{-8}$  M HCl is equal to 8.

**Explanation** : pH = 8 means basic solution. Contribution of water can not be neglected in this case.

7. **General Mistake** : If NaOH is added to  $\text{NH}_4\text{Cl}$  so that NaOH is limiting, the resulting solution is containing some remaining conc. of  $\text{NH}_4\text{Cl}$ . Now use salt hydrolysis condition to calculate pH of solution.

**Explanation** : The addition of NaOH in  $\text{NH}_4\text{Cl}$  results in a basic buffer solution.

8. **General Mistake** : Do not use the  $K_1 K_2$  form of equation unless you have an independent method of calculating  $[\text{H}^+]$  or  $[\text{S}^{2-}]$

**Explanation** : Determine the  $[\text{S}^{2-}]$  in a saturated  $\text{H}_2\text{S}$  solution to which enough HCl has been added to produce a  $[\text{H}^+]$  of  $2 \times 10^{-4}$ .

$$\text{Sol. : } K_1 K_2 = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{(2 \times 10^{-4})^2 [\text{S}^{2-}]}{0.10} = 1.0 \times 10^{-21} \text{ or}$$

$$[\text{S}^{2-}] = \frac{1.0 \times 10^{-22}}{4 \times 10^{-8}} = 2.5 \times 10^{-15}.$$