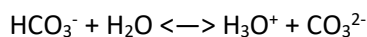
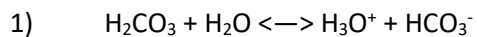


## Revision of basic concepts

### 1) Acid-base reactions: proton transfer

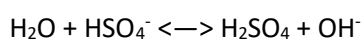
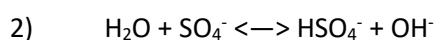
#### 1.a. Exercises on Key Concepts

##### Definitions according to Brønsted-Lowry



Acid

Conjugate Base

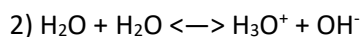


Base

Conjugate Acid

### Protolysis of water

1) A small fraction of water molecules dissociate to hydroxide ion ( $\text{OH}^-$ ) and hydronium ion ( $\text{H}_3\text{O}^+$ ) which, even in low concentrations ( $10^{-7} \text{ M}$ ), are capable of conducting current.



Acide + Base  $\rightleftharpoons$  Conjugate Acid + Conjugate Base

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$  is called the ion product of water

### Strength of an acid and a base

- 1) (a) Lactic acid ( $K_a = 1.4 \times 10^{-4}$ ) **X**  
(b) Propionic acid ( $K_a = 1.4 \times 10^{-5}$ ) **X**  
(c) Acetic acid ( $K_a = 1.8 \times 10^{-5}$ ) **X**  
(d) Pyruvic acid ( $K_a = 3.2 \times 10^{-3}$ ) **✓**

2)

$$K_w = K_a \times K_b$$

$$-\log K_w = -\log (K_a \times K_b)$$

$$14 = -\log K_a + -\log K_b \quad (\text{with } \text{p}K_a = -\log K_a \text{ and } \text{p}K_b = -\log K_b)$$

$$\text{p}K_a + \text{p}K_b = 14$$

(a) Lactic acid  $\text{p}K_a = 3.85$  therefore  $\text{p}K_b = 10.15$

(b) Propionic acid  $\text{p}K_a = 4.85$  therefore  $\text{p}K_b = 9.15$

(c) Acetic acid  $\text{p}K_a = 4.74$  therefore  $\text{p}K_b = 9.26$

(d) Pyruvic acid  $\text{p}K_a = 2.49$  therefore  $\text{p}K_b = 11.51$

The higher the  $pK_a$ , the lower the  $pK_b$ , so the weaker the acid, the stronger its conjugate base.

### Definition of pH

- 1) (a)  $pH = -\ln [H_3O^+]$  X
- (b)  $pH = \log [H_3O^+]$  X
- (c)  $pH = \log (1/[H_3O^+])$  ✓
- (d)  $pH = -\log (10^{-14} / [OH^-])$  ✓
- (e)  $pH = -\log ([H_3O^+])$  ✓

$$2) \quad pH = -\log ([H_3O^+]) \text{ and } [H_3O^+] = K_w / [OH^-]$$

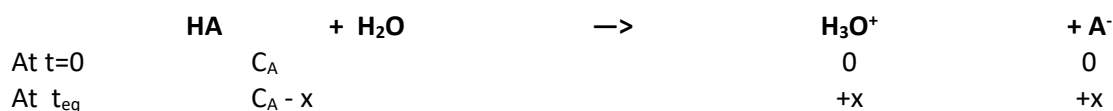
hence  $pH = -\log (10^{-14} / [OH^-])$  we get  $[OH^-] = 10^{-8} \text{ M}$

$$pH = -\log (10^{-14} / 10^{-8})$$

$$pH = 6$$

- 3) Weak acids and weak bases do not fully dissociate in solution.

The acid in the presence of water will dissociate according to the equation :



$$\text{This gives : } K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{C_A - x} \text{ or } x = [H_3O^+]$$

as the dissociation of the acid is weak, we can consider that  $x \ll C_A$ , so we can simplify by

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{C_A}$$

$$\text{so } x = [H_3O^+] = \sqrt{K_a C_A}$$

$$-\log ([H_3O^+]) = -\log (K_a C_A)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2} \log K_a - \frac{1}{2} \log C_A$$

$$pH = \frac{1}{2} (pK_a - \log C_A)$$

Using the same reasoning for the weak base, we obtain

$$x = [OH^-] = \sqrt{K_b C_B}$$

$$\text{so } [H_3O^+] = \frac{K_w}{\sqrt{K_b C_B}}$$

$$pH = 14 + \frac{1}{2} \log K_b + \frac{1}{2} \log C_B$$

$$pH = 14 + \frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log C_B$$

$$\text{pH} = 7 - \frac{1}{2} \log K_a + \frac{1}{2} \log C_B$$

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a + \log C_B)$$

### 1.b. Calculating the pH of acid solutions

1) Hydrochloric acid is a strong acid so  $[\text{H}_3\text{O}^+] = n_{\text{HCl}} V_{\text{HCl}} / V_{\text{sol}}$

$$[\text{H}_3\text{O}^+] = (1 \times 10^{-3} \times 1) / 1,001$$

$$[\text{H}_3\text{O}^+] = 9,9 \times 10^{-4} \text{ M}$$

$$\text{pH} = 3$$

2) These 3 acids are weak acids, so we use the relationship  $\text{pH} = \frac{1}{2} (\text{p}K_A - \log C_A)$

$$\text{with } \log C_A = \log (10^{-2}) = -2$$

$$\text{Lactic acid: } \text{pH} = (3.85 + 2) = 2.93$$

$$\text{Pyruvic acid: } \text{pH} = (2.49 + 2) = 2.25$$

$$\text{Acetic acid: } \text{pH} = (4.74 + 2) = 3.37$$

### 1.c. Calculating the pH of basic solutions

1) Sodium hydroxide, NaOH, is a strong base, completely dissociated into  $\text{Na}^+$  and  $\text{OH}^-$ , so

$$\text{pH} = -\log \left( \frac{K_w}{[\text{OH}^-]} \right) = -\log \left( \frac{10^{-14}}{5 \times 10^{-3}} \right)$$

$$\text{pH} = 11.7$$

2) These 3 conjugated bases are weak (based on the  $K_b$  values calculated) above. We can write:

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a + \log C_B)$$

$$\text{Lactic acid: } \text{pH} = 7 + (3.85 - 2) = 7.93$$

$$\text{Pyruvic acid: } \text{pH} = 7 + (2.49 - 2) = 7.25$$

$$\text{Acetic acid: } \text{pH} = 7 + (4.74 - 2) = 8.37$$

## 2) Oxidation-reduction reactions: electron transfer

### 2.a. Exercises on Key Concepts

#### Definition of a redox couple

1) A reductant is a chemical compound (molecule or ion) which is able to give up one or more electrons ( $e^-$ ). A reductant loses one or more electrons to become oxidized. This is called an oxidation reaction.

An oxidant is therefore a chemical compound (molecule or ion) that is capable of acquiring one or more electron(s). An oxidant acquires one or more electrons and becomes reduced. This is called a reduction reaction.

2) Each redox couple is assigned a standard electrochemical potential  $E^\circ$  (V) defined in relation to the couple  $H^+/H_2$  ( $E^\circ_{H^+/H_2} = 0.0V$ ). The oxidizing power decreases with decreasing potential.

3)

| Reactions                                        | Ox1       | Red1    | Ox2       | Red2    |
|--------------------------------------------------|-----------|---------|-----------|---------|
| $Cu(s) + 2AgNO_3 \rightarrow Cu(NO_3)_2 + Ag(s)$ | $Ag^+$    | $Cu(0)$ | $Cu^{2+}$ | $Ag(0)$ |
| $3Cl_2 + 2Al(s) \rightarrow 6Cl^- + 2Al^{3+}$    | $Cl_2(0)$ | $Al(0)$ | $Al^{3+}$ | $Cl^-$  |

### 2.b. Equilibrating redox reactions

1)  $NO_2^- + MnO_4^- + H_3O^+ \rightarrow NO_3^- + Mn^{2+} + H_2O$

-Determination of the pairs involved in the reaction

$MnO_4^- / Mn^{2+}$  et  $NO_3^- / NO_2^-$

-Determination of oxidation numbers and half-reactions

$MnO_4^-$  : N.O. = +VII

$Mn^{2+}$  : N.O. = +II

This reaction requires  $5e^-$  and the charges are balanced by  $H^+$ :

$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$  eq (1)

$NO_3^-$  : N.O. = +V

$NO_2^-$  : N.O. = +III

This reaction requires  $2e^-$  and the charges are balanced by  $H^+$ :

$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O$  eq (2)

-Electronic transfer equilibration : x2 for eq (1) and x5 for eq (2)

$2 MnO_4^- + 10 e^- + 16 H^+ \rightarrow 2 Mn^{2+} + 8 H_2O$

$5 NO_2^- + 5 H_2O \rightarrow 5 NO_3^- + 10 e^- + 10 H^+$

-Combination of the 2 equations

$5 NO_2^- + 2 MnO_4^- + 6 H^+ \rightarrow 5 NO_3^- + 2 Mn^{2+} + 3 H_2O$

ou  $5 NO_2^- + 2 MnO_4^- + 6 H_3O^+ \rightarrow 5 NO_3^- + 2 Mn^{2+} + 9 H_2O$

### 3) Precipitation/dissolution reactions

$M_nX_m(s) \leftrightarrow nM(aq) + mX(aq)$

$$K_s = [M]^n[X]^m \text{ and } S = \sqrt[n+m]{\frac{K_s}{n^n m^m}}$$

|     |                     |                                                       |                              |
|-----|---------------------|-------------------------------------------------------|------------------------------|
| (a) | CaCO <sub>3</sub>   | K <sub>s</sub> = 3.3*10 <sup>-9</sup> M <sup>2</sup>  | S = 5.75*10 <sup>-5</sup> M  |
| (b) | Mn(OH) <sub>2</sub> | K <sub>s</sub> = 2.0*10 <sup>-13</sup> M <sup>3</sup> | S = 3.68*10 <sup>-5</sup> M  |
| (c) | Cu(OH) <sub>2</sub> | K <sub>s</sub> = 4.8*10 <sup>-20</sup> M <sup>3</sup> | S = 2.28*10 <sup>-7</sup> M  |
| (d) | CdS                 | K <sub>s</sub> = 1.0*10 <sup>-27</sup> M <sup>2</sup> | S = 3.16*10 <sup>-14</sup> M |

CaCO<sub>3</sub> is the most soluble.