

# ACID-BASE EQUILIBBIUM

- *pH* and  $K_a$  revisited
- The definition

$$pH = -\log[H^+]$$

- is not exact.
- A better definition is

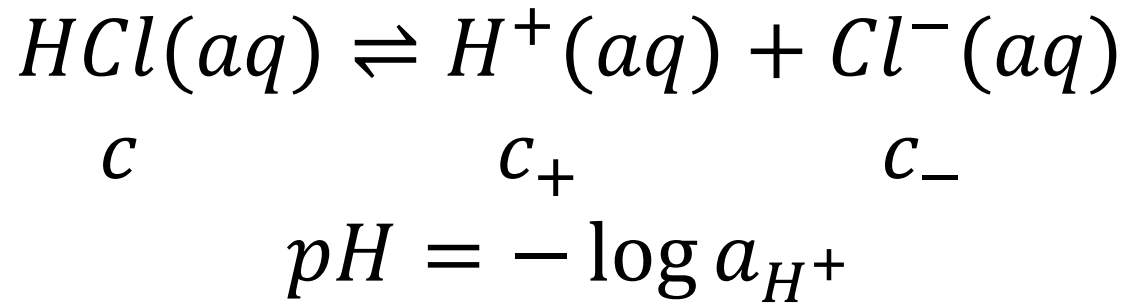
$$pH = -\log a_{H^+}$$

- When we measure pH with a pH meter, we are measuring the negative logarithm of the **hydrogen ion activity**, not concentration

# pH of an acid/base

## a) Strong acid

- Consider the dissociation of a strong acid HCl of concentration  $c$



But

$$a_i = \gamma_i \frac{c_i}{c^0} = \gamma_i c_i: \quad \text{since, } c^0 = 1 \frac{\text{mol}}{\text{L}}$$

Hence

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

$$\gamma_{\pm}^2 = \gamma_+ \gamma_-$$

$$\gamma_{\pm} = \gamma_+ = \gamma_-$$

$$pH = -\log c_+ \gamma_+ = -\log c_+ \gamma_{\pm}$$

$$= -\log c_+ + \log \gamma_{\pm}$$

$$= -[\log c_+ - 0.509 |z_+ z_-| \sqrt{I}]$$

$$= -[\log c_+ - 0.509 |1(-1)| \sqrt{I}]$$

$$= -\log c_+ + 0.509 \sqrt{I}$$

$$= -\log c_+ + 0.509 \sqrt{c}$$

# Example

- Calculate the pH of 0.01 M HCl

$$pH = -\log c_+ + 0.509 |z_+ z_-| \sqrt{I}$$

$$\begin{aligned} c_+ = c = 0.01 & \quad \text{and} \\ I = c & \quad \text{(for a 1:1 electrolyte)} \end{aligned}$$

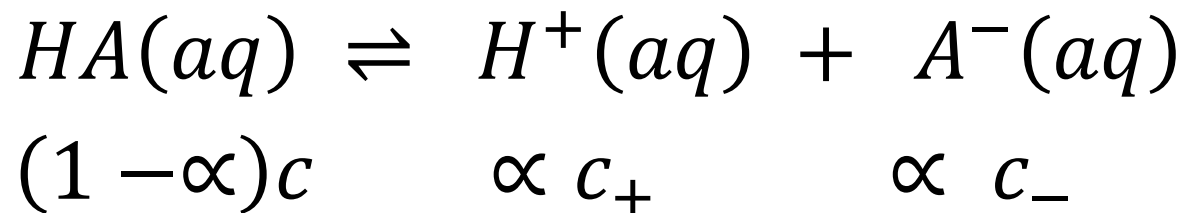
$$pH = -\log 0.01 + 0.509 |1(-1)| \sqrt{0.01}$$

$$pH = 2.00 + 0.0509$$

$$pH = 2.0509$$

## b) Weak acid

- Consider the dissociation of a weak acid HA of concentration  $c$



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

$$pH = -\log \alpha c_+ \gamma_+ = -\log \alpha c_+ \gamma_{\pm}$$

$$pH = -\log \alpha c_+ + \log \gamma_{\pm}$$

but

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

$$I = \frac{1}{2} \sum_{i=1}^n v_i c_i z^2$$

$$I = \frac{1}{2} [(1 \times \alpha c_+ \times (+1)^2) + (1 \times \alpha c_- \times (-1)^2)]$$

$$I = \frac{1}{2} \times 2(\alpha c)$$

$$I = (\alpha c)$$

So that

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{\alpha c}$$

And

$$pH = -\log \alpha c_+ + 0.509 |z_+ z_-| \sqrt{\alpha c}$$

# Example

- Consider a 0.0010M  $\text{CH}_3\text{COOH}$  has degree of dissociation of 0.134 and  $K_a$  of  $1.8 \times 10^{-5}$ 
  - a) Calculate pH of the solution
  - b) Determine the mean ionic activity coefficient using DHLL law

a)

$$pH = -\log \alpha c_+ + 0.509 |z_+ z_-| \sqrt{\alpha c}$$

$$\alpha c = 0.134 \times 0.001 = 1.34 \times 10^{-4}$$

$$pH = -\log 1.34 \times 10^{-4} + 0.509 |1 \times -1| \sqrt{1.34 \times 10^{-4}}$$

$$= 3.87 + 0.00589$$

*ideal*

$$= 3.87589$$

*non - ideal*

b)

$$\log \gamma_{\pm} = -0.509 I z_+ z_- I \sqrt{\alpha c}$$

$$\log \gamma_{\pm} = -0.509 I 1 \times -1 I \sqrt{1.34 \times 10^{-4}}$$

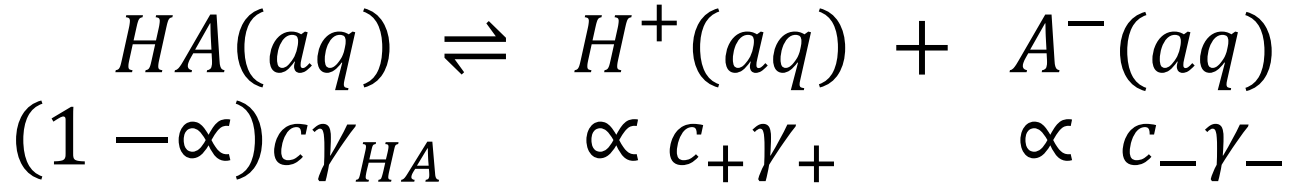
$$= -5.892 \times 10^{-3}$$

$$\gamma_{\pm} = 10^{-5.892 \times 10^{-3}}$$

$$= 0.9865$$

# Determination of $K_a$ of weak acid

- Consider the dissociation of the weak acid HA



- The equilibrium constant  $K_a$  is given by

$$K_a = \frac{(a_{H^+})^1 (a_{A^-})^1}{(a_{HA})^1} = \frac{(\alpha c_+\gamma_+)^1 (\alpha c_-\gamma_-)^1}{((1 - \alpha)c\gamma_{HA})^1}$$

$$K_a = \frac{(\alpha c)^2 \gamma_{\pm}^2}{(1 - \alpha)c\gamma_{HA}}$$

- $\gamma_{HA}$  is the activity coefficient for the undissociated acid.

- Since the undissociated acid is a nonelectrolyte, its activity coefficient is close to unity in dilute solutions and may be taken as unity to a good approximation.

$$K_a = \frac{(\alpha c)^2 \gamma_{\pm}^2}{(1 - \alpha)c}$$

$$\log K_a = \log \frac{\alpha^2 c}{(1 - \alpha)} + 2 \log \gamma_{\pm}$$

*ideal + non - ideal*

- but for a 1:1 electrolyte

$$\log \gamma_{\pm} = -0.509 \sqrt{\alpha c}$$

- hence

$$\log \frac{\alpha^2 c}{(1-\alpha)} = \log K_a + 2(0.509 \sqrt{\alpha c})$$

$$\log \frac{\alpha^2 c}{(1-\alpha)} = \log K_a + 1.018 \sqrt{\alpha c}$$

$$y = a + bx$$

$$x = \sqrt{\alpha c}$$

- $\alpha$  can be determined from conductance expts (to be discussed later, see chapter 8 Barrow)

$$\alpha = \frac{\Lambda_m}{\Lambda_m^o}$$