برهان علاقات الوحدة 4:

① في حالة تفاعل حمض ضعيف في الماء:

$AH + H_2O = A^- + H_3O^+$

	AH	$+ H_2O =$	A^-	$+ H_3O^+$
t_0	$C_A \cdot V_A$	/	0	0
t	$C_A V_A - x$	/	x	x
t_f	$C_A V_A - x_f$	/	x_f	x_f

① $\tau_f = \frac{x_f}{x_{max}}$ نظرية ليم بنية $= \frac{[H_3O^+]_f}{C_A} = \frac{10^{-pH}}{C_A}$

⇐ تعفظ و تبرهن.

↓ لدينا:

$$\tau_f = \frac{x_f}{x_{max}}$$

- نفرض أن التفاعل تام:

* AH متفاعل معدوم:

$$C_A \cdot V_A - x_{max} = 0$$

$$x_{max} = C_A \cdot V_A$$

ولدينا:

$$n_f(H_3O^+) = x_f$$

$$[H_3O^+]_f \cdot V_A = x_f$$

$$x_f = [H_3O^+]_f \cdot V_A$$

$$\tau_f = \frac{[H_3O^+] \cdot V_A}{C_A \cdot V_A} = \tau_f = \frac{[H_3O^+]_f}{C_A}$$

$$\tau_f = \frac{10^{-pH}}{C_A}$$

لأن:

$$pH = -\log[H_3O^+]$$

$$[H_3O^+] = 10^{-pH}$$

② $K = Ka = \frac{[H_3O^+]_f^2}{C_A - [H_3O^+]_f} = \frac{10^{-2pH}}{C_A - 10^{-pH}}$

لدينا:

$$K = \frac{[A^-]_f \cdot [H_3O^+]_f}{[AH]_f} = Ka.$$

بالنسبة للحمض:

$$K = Ka.$$

كما هو جدول التقدم:

- $[H_3O^+]_f = [A^-]_f$ ← تعفظ + تبرهن

- $[AH]_f = \frac{C_A \cdot V_A - x_f}{V_A} = \frac{C_A \cdot V_A}{V_A} - \frac{x_f}{V_A}$

$= C_A - [H_3O^+]_f$ ← تعفظ + تبرهن

بالتعويض:

$$K = Ka = \frac{[H_3O^+]_f^2}{C_A - [H_3O^+]_f} = \frac{(10^{-pH})^2}{C_A - 10^{-pH}}$$

$$= \frac{10^{-2pH}}{C_A - 10^{-pH}}$$ ← تبرهن.

③ $Ka = \frac{\tau_f^2 \cdot C_a}{1 - \tau_f}$

لدينا:

$$Ka = \frac{[H_3O^+]_f \cdot [A^-]_f}{[AH]_f}.$$

ونعلم أن:

- $[H_3O^+]_f = [A^-]_f$ ... ①
- $[AH]_f = C_A - [H_3O^+]_f$ ... ②
- $\tau_f = \frac{[H_3O^+]_f}{C_A}$ ... ③

$$Ka = \frac{[H_3O^+]^2}{C_A - [H_3O^+]_f}.$$

$[H_3O^+]_f = \tau_f \cdot C_A$. من ③

① ②

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$\tau_f = \frac{x_f}{x_{max}} \Rightarrow \boxed{x_f = \tau_f \cdot x_{max}}$

بالتعويض:

$$K = K_a = \frac{\tau_f^2 \cdot x_{max}^2}{V_A(C_A \cdot V_A - \tau_f \cdot x_{max})}$$

نعلم أن: $\boxed{x_{max} = C_A \cdot V_A}$

$$K = K_a = \frac{\tau_f^2 \cdot x_{max}^2}{V_A(x_{max} - \tau_f \cdot x_{max})}$$

$$K = K_a = \frac{\tau_f^2 \cdot x_{max}^2}{V_A \cdot x_{max}(1 - \tau_f)}$$

$$K = K_a = \frac{\tau_f^2 \cdot x_{max}}{V_A(1 - \tau_f)}$$

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⑥ $pH = pK_a + \log \frac{[A^-]_f}{[AH]_f}$ صيغة مطابقة

علاقة أندرسون "تقطع وتبرهن"

لدينا:

$$K_a = \frac{[H_3O^+]_f \cdot [A^-]_f}{[AH]_f}$$

$pK_a = -\log K_a$

نأخذ log للطرفين:

$\log K_a = \log [H_3O^+] + \log \frac{[A^-]_f}{[AH]_f}$

نأخذ $-$ للطرفين:

$-\log K_a = -\log [H_3O^+] - \log \frac{[A^-]_f}{[AH]_f}$

$pK_a = pH - \log \frac{[A^-]_f}{[AH]_f}$

$pH = pK_a + \log \frac{[A^-]_f}{[AH]_f}$

$pK_a = pH \pm \log \frac{[AH]_f}{[A^-]_f}$ (+ قاعدي، − حمضي) : 2 ب

$$K_a = \frac{\tau_f^2 \cdot C_A^2}{C_A - \tau_f \cdot C_A}$$

ع.ع

$$= \frac{\tau_f^2 \cdot C_A^2}{C_A(1 - \tau_f)}$$

$$K_a = \frac{\tau_f^2 \cdot C_A}{1 - \tau_f}$$

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④ $K = K_a = \frac{x_f^2}{V_A(C_A \cdot V_A - x_f)}$

نعلم أن:

$$K = K_a = \frac{[H_3O^+]_f \cdot [A^-]_f}{V \cdot [AH]_f}$$

$$\begin{cases} [H_3O^+] = [A^-]_f = \frac{x_f}{V_A} \\ [AH]_f = \frac{C_A \cdot V_A - x_f}{V_A} \end{cases}$$

بالتعويض:

$$K_a = \frac{\left(\frac{x_f}{V_A}\right)\left(\frac{x_f}{V_A}\right)}{\frac{C_A \cdot V_A - x_f}{V_A}}$$

$$K_a = \frac{\left(\frac{x_f}{V_A}\right)^2}{C_A \cdot V_A - x_f}$$ (ضرب ÷ تعاكس)

$$K_a = \frac{x_f^2}{V_A(C_A \cdot V_A - x_f)}$$

5- $K = K_a = \frac{x_{max} \cdot \tau_f^2}{V_A(1 - \tau_f)}$

لدينا:

$$K = K_a = \frac{x_f^2}{V_A(C_A \cdot V_A - x_f)}$$

② لدينا:

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$$-\log \frac{[A^-]_f}{[AH]_f} = pKa - pH$$

نقلب ثم (الإشارات): (log العلاقة): نأخذ 10 أس

$$\frac{[AH]_f}{[A^-]_f} = 10^{pKa-pH}$$

نعلم أن:

$$[A^-] = [H_3O^+] = \tau_f \cdot c_a$$

$$[AH] = \frac{c_a \cdot V_a - \xi_f}{V_a} = c_a - [H_3O^+] = c_a - \tau_f \cdot c_a$$

$$= c_a(1-\tau_f)$$

$$\frac{c_a(1-\tau_f)}{\tau_f \cdot c_a} = 10^{pKa-pH}$$

تبسيط:

$$\frac{1-\tau_f}{\tau_f} = 10^{pKa-pH}$$

$$\frac{1}{\tau_f} - \frac{\tau_f}{\tau_f} = 10^{pKa-pH}$$

$$\frac{1}{\tau_f} - 1 = 10^{pKa-pH}$$

$$\frac{1}{\tau_f} = 10^{pKa-pH} + 1$$

بالمقلوب:

$$\tau_f = \frac{1}{1 + 10^{pKa-pH}}$$

⑨ -

$$\tau_f = \frac{Ka}{Ka + 10^{-pH}}$$

لدينا من علاقة .

$$Ka = \frac{[H_3O^+]_f \cdot [A^-]_f}{[AH]_f}$$

$$Ka = \frac{[H_3O^+]_f^2}{c_a \cdot [H_3O^+]_f}$$

$$Ka = \frac{c_a^2 \cdot \tau_f^2}{c_a(1-\tau_f)}$$

نعلم أن:

$$\tau_f = \frac{[H_3O^+]_f}{c}$$

ومنه:

$$[H_3O^+] = \tau_f \cdot c$$

طريقة أخرى:

$$Ka = \frac{[H_3O^+]_f^2}{[AH]_f}$$

بأخذ log

$$-\log Ka = -\log [H_3O^+] + \log [AH]$$

$$\boxed{pKa = 2pH + \log [AH]}$$

$$2pH = pKa - \log [AH]$$

$$\boxed{pH = \frac{1}{2} pKa - \frac{1}{2} \log [AH]}$$

⑦ -

$$pH = pKa + \log \left(\frac{\tau_f}{1-\tau_f} \right)$$

من علاقة أندرسون:

$$pH = pKa + \log \frac{[A^-]_f}{[AH]_f}$$

نعلم أن:

$$[A^-]_f = [H_3O^+]_f = \tau_f \cdot c_a$$

$$[AH]_f = c_A - [H_3O^+] = c_A - c_a \cdot \tau_f$$

$$= c_a(1-\tau_f)$$

بالتعويض:

$$pH = pKa + \log \left(\frac{\tau_f \cdot c_a}{c_a(1-\tau_f)} \right)$$

$$pH = pKa + \log \left(\frac{\tau_f}{1-\tau_f} \right)$$

⑧

$$\tau_f = \frac{1}{1 + 10^{pKa-pH}}$$

لدينا من علاقة أندرسون:

$$pH = pKa + \log \frac{[A^-]_f}{[AH]_f}$$

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$x_{max} = C_B \cdot V_B$ ---②

و

$x_f = n(OH^-)_f$

$[OH^-] \cdot V_B = x_f$

ومنه :

$\tau_f = \frac{[OH^-] \cdot V_B}{C_B \cdot V_B} = \frac{[OH^-]}{C_B}$

من الجداء الشاردي للماء :

$K_e = [H_3O^+] \cdot [OH^-] = 10^{-14}$

ونعلم أن :

$[H_3O^+] = 10^{-pH}$

ومنه :

$[OH^-] = \frac{K_e}{[H_3O^+]}$

$[OH^-] = \frac{10^{-14}}{10^{-pH}} \Rightarrow [OH^-] = 10^{pH-14}$

ومنه :

$\tau_f = \frac{10^{pH-14}}{C_B}$

(1) $\tau_f = \frac{K_e}{C_B} \times 10^{pH}$

لدينا :

$\tau_f = \frac{[OH^-]_f}{C_B} \times \frac{[H_3O^+]}{[H_3O^+]}$

نضرب في

$\tau_f = \frac{K_e}{C_B \cdot 10^{-pH}}$

ومنه :

$\tau_f = \frac{K_e}{C_B} \cdot 10^{pH}$

$K_a = \frac{\tau_f^2 \cdot C_a}{1 - \tau_f}$

نعلم أن :

$\tau_f = \frac{10^{-pH}}{C_a}$

$C_a = \frac{10^{-pH}}{\tau_f}$

$K_a = \frac{\tau_f^2}{1 - \tau_f} \cdot \frac{10^{-pH}}{\tau_f}$

$K_a = \frac{\tau_f \cdot 10^{-pH}}{1 - \tau_f}$

$\tau_f \cdot 10^{-pH} = K_a - K_a \tau_f$

$\tau_f \cdot 10^{-pH} + \tau_f K_a = K_a$

$K_a = \tau_f (10^{-pH} + K_a)$

$\tau_f = \frac{K_a}{10^{-pH} + K_a}$

II - انتقال أساسي في الماء :

	$B + H_2O = BH^+ + OH^-$			
t_0	$C_B \cdot V_B$	+	0	0
t	$C_B \cdot V_B - x$	+	x	x
t_f	$C_B \cdot V_B - x_f$	+	x_f	x_f

(10)

$\tau_f = \frac{10^{pH-14}}{C_B}$

$\tau_f = \frac{x_f}{x_{max}}$ ---④

بفرض التفاعل تام :

فإن B محد ، ومنه :

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(14) $\tau_f = \dfrac{1}{1 + Ka \cdot 10^{pH}}$

$Ka = \dfrac{[H_3O^+] \cdot [B]_f}{[BH^+]_f}$

$Ka = 10^{-pH} \cdot \dfrac{C_B(1-\tau_f)}{\tau_f \cdot C_B}$

بالتبسيط:

- $[B]_f = C_B - [OH^-]_f = C_B - \tau_f \cdot C_B$
  $= C_B(1-\tau_f)$
- $[BH^+]_f = [OH^-]_f = \tau_f \cdot C_B$

$\tau_f = \dfrac{[OH^-]_f}{C_B}$ ، $[OH^-]_f = \tau_f \cdot C_B$

$Ka = 10^{-pH} \cdot \dfrac{1-\tau_f}{\tau_f}$

$Ka = 10^{-pH} \cdot \left(\dfrac{1}{\tau_f} - 1\right)$

$\dfrac{Ka}{10^{-pH}} = \dfrac{1}{\tau_f} - 1$

ومنه:

$\dfrac{1}{\tau_f} = \dfrac{Ka}{10^{-pH}} + 1 = Ka \cdot 10^{+pH} + 1$

بالطرفين:

$\tau_f = \dfrac{1}{10^{pH} \cdot Ka + 1}$

(15) - $\tau_f = \dfrac{1}{1 + 10^{pH-pKa}}$

من علاقة أندرسون:

$pH = pKa + \log \dfrac{[B]_f}{[BH^+]_f}$

$pH - pKa = \log \dfrac{[B]_f}{[BH^+]_f}$

بالوصول: $\dfrac{[B]_f}{[BH^+]_f} = 10^{pH-pKa}$.

(12) - $K = \dfrac{Ke}{Ka}$

بالنسبة للأساس: $Ka \neq K$.

$K = \dfrac{[BH^+]_f \cdot [OH^-]_f}{[B]_f} \times \dfrac{[H_3O^+]}{[H_3O^+]}$

Ke ، $\dfrac{1}{Ka}$

$K = \dfrac{1}{Ka} \cdot Ke$

$K = \dfrac{Ke}{Ka} = \dfrac{10^{-14}}{10^{-pKa}} = 10^{pKa-14}$

(13) $\tau_f = \dfrac{K}{K + 10^{pH-14}}$

$K = \dfrac{[OH^-]_f \cdot [BH^+]_f}{[B]_f}$

نسبيا:

- $[BH^+]_f = [OH^-]_f = \tau_f \cdot C_B$.
- $[B^+]_f = C_B - [OH^-]_f = C_B - \tau_f \cdot C_B$
  $= C_B(1-\tau_f)$.

بالتعويض:

$K = \dfrac{\tau_f \cdot C_B \times 10^{pH-14}}{C_B(1-\tau_f)}$

$K = \dfrac{\tau_f \cdot 10^{pH-14}}{1-\tau_f}$

$K(1-\tau_f) = \tau_f \cdot 10^{pH-14}$.

$K - \tau_f K = \tau_f \cdot 10^{pH-14}$.

$K = \tau_f \cdot 10^{pH-14} + K \cdot \tau_f$

$K = \tau_f (10^{pH-14} + K)$.

$\tau_f = \dfrac{K}{K + 10^{pH-14}}$

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$$\tau_f = \frac{\sqrt{K}}{1+\sqrt{K}}$$

$$\tau_f = \frac{x_f}{x_{max}} < \frac{x_f}{n_0} \rightarrow x_f = \tau_f \cdot n_0$$

$$K = \frac{[A^-]_f \cdot [BH]_f}{[AH]_f \cdot [B]_f} = \frac{\frac{x_f^2}{V^2}}{\frac{(n_0 - x_f)^2}{V^2}}$$

$$K = \frac{x_f^2}{(n_0 - x_f)^2} = \frac{\tau_f^2 \cdot n_0^2}{(n_0 - \tau_f \cdot n_0)^2}$$

$$\sqrt{K} = \frac{\tau_f \cdot n_0}{n_0 - \tau_f \cdot n_0} = \frac{\tau_f \cdot n_0}{n_0(1-\tau_f)}$$

$$\sqrt{K} = \frac{\tau_f}{1-\tau_f}$$

$$\sqrt{K}(1-\tau_f) = \tau_f$$

$$\sqrt{K} - \sqrt{K}\tau_f = \tau_f$$

$$\sqrt{K} = \tau_f + \sqrt{K}\tau_f$$

$$\sqrt{K} = \tau_f(1+\sqrt{K})$$

$$\tau_f = \frac{\sqrt{K}}{1+\sqrt{K}}$$

$$\frac{C_B(1-\tau_f)}{\tau_f \cdot C_B} = 10^{pH-pK_a}$$

$$\frac{1-\tau_f}{\tau_f} = 10^{pH-pK_a}$$

$$\frac{1}{\tau_f} - 1 = 10^{pH-pK_a}$$

$$\frac{1}{\tau_f} = 10^{pH-pK_a} + 1$$

ومنه بالقلوب:

$$\tau_f = \frac{1}{1 + 10^{pH-pK_a}}$$

(16) - نحسب أساس ضعيف جدا في الماء

$$C_b = 10^{2pH - pK_a - pK_e}$$

نحسب أساس ضعيف جدا.

$1 - \tau_f = 1$

$[B]_f = C_b$ ⇐

منه حسب قانون:

$$pH = pK_a + \log\frac{[B]_f}{[BH^+]_f}$$

$$pH = pK_a + \log\frac{C_b}{[OH^-]_f} \times \frac{[H_3O^+]}{[H_3O^+]}$$

$$pH = pK_a + \log\frac{C_b \cdot 10^{-pH}}{K_e}$$

$$pH = pK_a + \log(C_b \cdot 10^{-pH}) - \log K_e$$

$$pH = pK_a + \log C_b - pH + pK_e$$

$$pH + pH - pK_a - pK_e = \log C_b$$

بأخذ $10^{\ }$ =

$$C_b = 10^{2pH - pK_a - pK_e}$$

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