How can we measure K_a from pH?

ex: pH of a 0.20M soln of $HC_6H_7O_6(aq)$ @25°C, pH = 2.40

What's its K_a?

$$HC_6H_7O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_7O_6^-(aq)$$

	$HC_6H_7O_6$		H_3O^+	$C_6H_7O_6^-$
I	0.20M	—	≈0	0
C	−x	—	+x	+x
E	(0.20 − x)	—	(x)	(x)

$$K_a = \frac{[H_3O^+][C_6H_7O_6^-]}{[HC_6H_7O_6]_{eq}}$$

$pH = -\log_{10}[H^+]$

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

2dp

2sf. $x = 10^{-2.40} = 4.0\times10^{-3}$

$$K_a \overset{?}{=} \frac{(x)(x)}{0.20-x}$$

$$\Rightarrow K_a = \frac{(4.0\times10^{-3})^2}{0.20-4.0\times10^{-3}} = 8.1\times10^{-5}$$

Monoprotic acid: 1 H^+/molecule : HCl

Diprotic acid: 2 H^+/molecule : H_2SO_4

Polyprotic acid: >1 H^+/molecule

ex: oxalic acid : $H_2C_2O_4$

$K_{a1} = 6.5\times10^{-2}$

$$H_2C_2O_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-(aq)$$

$K_{a2} = 6.1\times10^{-5}$

$$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq)$$

in general: $K_{a1} > K_{a2} > K_{a3} > \ldots$

→ successively smaller

Weak Bases

acids, HA

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$ (H^+ transfer; K_a)

weak bases, B

$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$ (H^+ transfer; K_b)

$$K_b = \frac{[BH^+][OH^-]}{[B]_{eq}}$$

ex: Ammonia is a weak base,

$K_b = 1.8 \times 10^{-5}$ @25 °C.

What's pH of a 0.50 M sol'n?

ICE-Chart

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (H^+ transfer)

	NH_3		NH_4^+	OH^-
I	0.50M	—	0	≈0
C	$-x$	—	$+x$	$+x$
E	$(0.5-x)$	—	(x)	(x)

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]_{eq}}$$

pH?

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.5-x}$$

Assume: $x \ll 0.5$

$$1.8 \times 10^{-5} \cong \frac{(x)(x)}{0.50}$$

$$\Rightarrow \sqrt{(1.8 \times 10^{-5})(0.5)} = \sqrt{x^2} = x$$

$\Rightarrow x = 3.0 \times 10^{-3}$

Check Assumption: 5% rule.

<5% dissociated ✓

$$\% \text{ dissoc.} = \frac{[OH^-]_{eq}}{[B]_0} \times 100 \quad (x \text{ is } [OH^-]_{eq})$$

$$= \frac{3 \times 10^{-3} M}{0.50 M} \times 100$$

$$= 0.6\% \quad (2 \text{ s.f.}) \quad ✓$$

$\Rightarrow [OH^-] = 3.0 \times 10^{-3} M$

$pOH = -\log_{10}[OH^-]$

$= 2.52$ (2 dp)

$\Rightarrow pH = 14.00 - pOH = 11.48$

$\Rightarrow pH + pOH = 14.00$ (25°C) BASIC

Conjugate ACID-BASE pairs

HA / A^-

acid / base

ex: HF/F^-

conjugate

B / BH^+ $\quad NH_3 / NH_4^+$

base / acid

conjugate

K_a and K_b for conj. pairs are related!

$$\boxed{K_a \cdot K_b = K_w}$$ at any temp

ex. HCN — CN^-

hydrocyanic acid — cyanide

$K_a = 4.9 \times 10^{-10}$ @ 25°C

$K_a \cdot K_b = K_w$

$K_b = \frac{K_w}{K_a}$

$= \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}}$

$= 2.0 \times 10^{-5}$