18.2 Calculations w/ A & B

Ionization of H_2O

Kw is temp dependent (since eqm constant)

* $H_2O \rightleftharpoons H^+ + OH^-$ endothermic (breaking bonds)
  - ↑ Temp = shifts right, Kw ↑'s
  - ↓ Temp = shifts left, Kw ↓'s

Change Kw, change $[H^+]$ & $[OH^-]$ ∴ change pH
table pg 367

* even though pH changes H_2O is still neutral b/c $[H^+]$ & $[OH^-]$ are always equal

pH & pOH scales are interrelated

* $pOH = -\log[OH^-]$ vs. $pH = -\log[H^+]$
  - $[OH^-] = 10^{-pOH}$ $[H^+] = 10^{-pH}$

- inverse relationship
- scales inverse

* ↑ $[H^+]$ ↓ $[OH$
  - ↑ $[H^+]$ ↓ pH v/v OH

* if K_w $(1.00 \times 10^{-14}) = [H^+][OH^-]$ at 298 K
  - then, $pH + pOH = pK_w$ (14.00)

(graphs 368/369)

ex: lemon juice pH = 2.90 @ 298 K

$[H^+] = 10^{-pH} = 10^{-2.90} = \boxed{1.26 \times 10^{-3} \text{ mols dm}^{-3}}$

$pH + pOH = 14 \quad pOH = 14 - pH = 14 - 2.90 = \boxed{11.10}$

$[OH^-] = 10^{-pOH} = 10^{-11.10} = \boxed{7.94 \times 10^{-12} \text{ mols dm}^{-3}}$

or

$K_w = [H^+][OH^-] = 1.00 \times 10^{-14} = (1.26 \times 10^{-3})(OH^-) =$

Strong A/B → pH/pOH deduced from [I]

b/c assume full dissociation [I] = [eqm]

Calc pH:

1) $NaOH \rightarrow Na^+ + OH^-$ → $pOH = -\log(0.10) = 1$

	NaOH	Na^+	OH^-
[I]	0.10	0	0
[eqm]			0.10

$pOH + pH = 14$

$\boxed{pH = 13}$

2) $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ $pH = -\log(0.30) = 0.52$

	H_2SO_4	$2H^+$	SO_4^{2-}
[I]	0.15	0	0
[eqm]		2(0.15) = 0.30	

Weak A/B → do not fully dissociate ∴ reach eqm

need to write eqm expression to determine $[H^+]$ / $[OH^-]$

* 1 $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

* 2 $Ka = \frac{[H_3O^+][A^-]}{[HA]}$ - modified[3] eqm constant → acid dissociation constant (measure of dissociation aka strength)

4 ★ does not depend on [acid]

5 fixed value for particular acid at specified temp

↑ Ka, stronger acid, b/c more dissociation ∴ more product made

$B + H_2O \rightleftharpoons BH^+ + OH^-$

$K_b = \frac{[BH^+][OH^-]}{[B]}$ - base dissociation constant

↑ K_b, ↑ base strength b/c more dissociation

Ka + Kb allow: 1) compare strengths of weak A/B
2) calc [ion] at eqm
3) pH + pOH calc

ICE calculations 1) given [I] → before dissociation
2) pH/pOH → $[H^+]/[OH^-]$ at eqm
3) [eqm] go into expression
4) small Ka/Kb - use approximations

2 do examples pg 373-374

due to small #'s K_a + K_b → pK_a + pK_b

★ $pK_a = -\log K_a$ vs $pK_b = -\log K_b$
$K_a = 10^{-pK_a}$ $K_b = 10^{-pK_b}$

- pK_a/pK_b usually positive + no units
- inverse relationship

strong acid
K_a↑ ↑ ↓ pK_a↑
weak acid

- change of 1 pK_a/pK_b = 10-fold change K_a/K_b
- pK_a/pK_b @ specified temp → table 21
(need to convert to K_a/K_b for calcs)

★ $K_a \times K_b = [H^+][OH^-] = K_w$
∴ $pK_a + pK_b = pK_w$ (14) → holds for any conjugate A/B pair

↑ K_a, ↓ K_b (for conj. base)
∴ stronger acids have weaker conj. bases

$$K_a \times K_b = \frac{[H^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$ } for conj. A/B