ACID-BASE EQUILIBRIUM

1: EQUILIBRIUM CONSTANT K_a , K_b AND pH

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ACID BASE EQUILIBRIUM

Acid base **equilibrium** occurs when we deal with **weak acids and bases.** There is incomplete ionization of the acid.

We can write an acid equilibrium reaction for the generic acid, HA.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Acetic acid is a weak acid. It reacts with water as follows (HA = $HC_2H_3O_2$)*

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_2H_3O_2{}^-_{(aq)}$$

Equilibrium constant, K_c can be calculated as in any equilibria (products over reactants); however here K_c is referred to as K_a as it is specific for acids. Water is not part of the equilibrium as water is a liquid and has no concentration.

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Note: the higher the K_a value – the more the concentration of hydronium ion and the stronger the acid.

**Acetic acid can also be written as $CH_3COO\mathbf{H}$, but then the acidic proton is the last one, so it is more convenient to write it as $\mathbf{H}C_2H_3O_2$.*

K_a FOR WEAK ACIDS

Acid ionization Constants at 25 °C

Acid	Formula	Constant K_a
Acetic acid	$HC_2H_3O_2$	1.7×10^{-5}
Benzoic acid	$HC_7H_5O_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
	HBO_3	4.8×10^{-11}
Cyanic acid	HOCN	3.5×10^{-4}
Formic acid	$HCHO_2$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-2}
Hydrogen sulfate ion	HSO_4^-	1.1×10^{-4}
Hydrogen sulfide	H_2S	8.9×10^{-4}
	HS^-	1.2×10^{-13}

EXAMPLE 1: QUICK CHECK: K_a FOR SOME ACIDS

You have prepared dilute solutions of equal molar concentrations of $HC_2H_3O_2$ (acetic acid), HNO_2, HF, and HCN. Rank the solutions from the highest pH to the lowest pH using the K_a values given.

Answer:

Acid	K_a	pH
HF	6.8×10^{-4}	**highest**
HNO_2	4.5×10^{-4}	
$HC_2H_3O_2$	1.7×10^{-5}	
HCN	4.9×10^{-10}	**lowest**

CALCULATIONS USING K_a

From the K_a values and concentrations of acids, one can calculate the concentrations of all ions at equilibrium, and then the pH of the acid.

- Remember in weak acids and bases, the ionization is not complete, so not all the hydronium ions will be in solution.
- If the pH of the solution is given, then *x* or concentration of product ions can be calculated from it.
- This setup is similar to equilibrium setup. Remember again that water is not part of the equilibrium as it is a liquid. (*I may not be writing water in future equations*).

	$HA_{(aq)}$	$H_2O_{(l)}$ $\rightleftharpoons$	$H_3O^+{}_{(aq)}$	$A^-{}_{(aq)}$
Initial	C_1		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$C_1 - x$		x	x

EXAMPLE 2: CALCULATING pH

Calculate the pH of a 0.18 *M* solution of a weak acid that has $K_a = 9.2 \times 10^{-6}$.

Answer:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

	$HA_{(aq)}$	$H^+_{(aq)}$	$A^-_{(aq)}$
Initial	0.18 M	0	0
Change	$-x$	$+x$	$+x$
At Eq.	$0.18-x$	x	x

$$9.2 \times 10^{-6} = \frac{(x)(x)}{0.18\ \text{M} - x}$$

$$9.2 \times 10^{-6} = \frac{x^2}{0.18\ M}$$

$$x = \sqrt{(9.2 \times 10^{-6})(0.18)} = 1.29 \times 10^{-3}\text{M}$$

$$1.29 \times 10^{-3} M = x$$

$$\text{pH} = -\log(1.3 \times 10^{-3}\text{M}) = 2.89$$

Do we ignore *x*?

$$\frac{0.18\ M}{9.2 \times 10^{-6}} > 100, \text{so } yes, ignore\ x$$

Check % ionization to make sure ignoring *x* was valid.

$$\frac{1.3 \times 10^{-3} M}{0.18\ M} \times 100 = 0.72\%$$

$0.72\% < 5\%$

So ignoring *x* was okay

WHEN TO IGNORE X

For the equilibrium conc. of C_1 (C_1-x); x can usually be ignored because in weak acids and bases "*x*" is very small. To know when to ignore *x* use either of the two equations below. (*I prefer the first one*).

- Divide the molarity (M) of the **initial** acid/base solution by the K_a or K_b. If value is more than 100 then ignore *x*.

$$\frac{M}{K_a} > 100$$

- Alternatively, you can also use the formula below for percent ionization **after** you have calculated the molarity of the solution. If the percent ionization is less than 5% then ignoring *x* was fine.

$$\frac{K_a}{M} \times 100\% < 5\%$$

- Another clue is that if K_a or K_b 10^{-5} or less then don't worry with calculations, just ignore *x*.

EXAMPLE 3: CALCULATING pH

Para–hydroxybenzoic acid is used to make certain dyes. What are the concentrations of this acid, of hydronium ion, and of para–hydroxybenzoate ion in a **0.200 M** aqueous solution at 25 °C? What is the pH of the solution? The K_a of this acid is $\mathbf{2.6 \times 10^{-5}}$.

Answer: (use HA as a generic acid)

$$HA_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Initial	0.200	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	0.200 – x	x	x

Step 1 Do we ignore x?

$$\frac{0.200\ M}{2.6 \times 10^{-5}} > 100, \text{so } yes, ignore\ x$$

Step 2

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

$$2.6 \times 10^{-5} = \frac{x^2}{0.200 - x}$$

$$2.6 \times 10^{-5} = \frac{x^2}{0.200}$$

$$2.6 \times 10^{-5} \times 0.200 = x^2$$

$$x = \sqrt{(2.6 \times 10^{-5})(0.2)} = 2.3 \times 10^{-3}\text{M}$$

$[H_3O^+] and\ [A^-]$

$$0.200 - 2.6 \times 10^{-3} = 0.197\ \text{M}\ [HA]$$

$$\text{pH} = -\log(2.3 \times 10^{-3})$$

$$\text{pH} = 2.64$$

EXAMPLE 4: CALCULATING K_a, % IONIZATION

Sore–throat medications sometimes contain the weak acid phenol, HC_6H_5O. A **0.10** ***M*** solution of phenol has a pH of **5.43** at 25 °C.

a) What is the acid–ionization constant, K_a, for phenol at 25 °C?

b) What is the degree of ionization?

Answer:

	$HC_6H_5O_{(aq)} \rightleftharpoons$	$H_3O^+_{(aq)}$ +	$C_6H_5O^-_{(aq)}$
Initial	0.10	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	x

a) If pH = 5.43 then $[H_3O^+] = 3.7 \times 10^{-6}$ *M* = x = $[C_6H_5O^-]$.

$[HC_6H_5O] = 0.10 - x = 0.10$ *M. (x is a very small amount so it's subtraction from the original conc. will give almost the same original conc.)*

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EXAMPLE 4: CONTD…

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$$HC_6H_5O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + C_6H_5O^-_{(aq)}$$

$$[HC_6H_5O] = 0.10\ M \qquad [H_3O^+] = [C_6H_5O^-] = 3.7 \times 10^{-6}\ M$$

Once we have all the values we can calculate K_a.

$$K_a = \frac{[H_3O^+]\,[C_6H_5O^-]}{[HC_6H_5O]} = \frac{(3.7 \times 10^{-6})^2}{0.10}$$

$$K_a = 1.4 \times 10^{-10}$$

b) Degree of ionization is ratio of ionized to original concentrations.

$$\text{Degree of ionization} = \frac{x}{0.10} \times 100\% = \frac{3.7 \times 10^{-6}}{0.10} \times 100\% = 3.7 \times 10^{-3}\,\%$$

CALCULATING pH FOR WEAK BASES

The degree to which a weak base ionizes depends on

- the concentration of the base.
- the equilibrium constant for the ionization called the base ionization constant, K_b. H_2O is the acid here.

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

- Solving for x gives the hydroxide ion conc. – **not** the hydronium ion conc., so one more calculation is needed to get the pH: calculate $[H_3O^+]$ using K_w.
- Example of some weak base equations:

Ammonia becomes ammonium ion: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Ethylamine becomes ethyl ammonium ion: $C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$

K_b FOR WEAK BASES

Base ionization Constants at 25 ^{o}C.

Base	Formula	Constant K_b
Ethylamine	$C_2H_5NH_2$	5.6×10^{-4}
Methylamine	CH_3NH_2	4.5×10^{-4}
Ammonia	NH_3	1.8×10^{-9}
Pyridine	C_5H_5N	1.7×10^{-10}
Aniline	$C_6H_5NH_2$	3.8×10^{-10}
Urea	H_2NCONH_2	1.5×10^{-14}

EXAMPLE 5: CALCULATE pH FOR WEAK BASE

Calculate the pH of a 0.0142 M weak base with K_b of 5.6 x 10^{-6} at 25 °C.

Answer: $B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$

Initial	0.0142		0	0
Change	$-x$		$+x$	$+x$
Eq.	$0.0142 - x$		x	x

$K_b = \frac{[HB^+][OH^-]}{[B]}$

Step 1 $5.6 \times 10^{-6} = \frac{x^2}{0.0142 - x}$

$5.6 \times 10^{-6} \times 0.0142 = x^2$

$x = \sqrt{(5.6 \times 10^{-6})(0.0142)} = 2.82 \times 10^{-4}\text{M}$

$= [OH^-]$

Step 2 Do we ignore x?

$\frac{0.0142M}{5.6 \times 10^{-6}} = 2535 > 100, ignore\ x$

Step 3 Two ways to do calculate pH: either calc. $[H_3O^+]$ using K_w or calc pOH.

$K_w = [H_3O^+][OH^-]$ $[H_3O^+] = \frac{1 \times 10^{-14}}{2.82 \times 10^{-4}} = 3.546 \times 10^{-11}$ $pH = -\log(1.258 \times 10^{-6}) = \boxed{10.5}$

OR $pOH = -\log(2.82 \times 10^{-4}) = 3.55$ $pH = 14 - pOH = 14 - 3.55 = \boxed{10.5}$

EXAMPLE 6: CALCULATE K_b

Determine the K_b of a weak base if a 0.350 *M* solution of the base has a pH of 10.6 at 25°C.

Answer:

pOH = 14.00-10.6 = 3.4 $[OH^-] = 10^{-3.4} = 3.89 \times 10^{-4}$M

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$$

Initial	0.350 M		
Change	-3.89×10^{-4} M	$+3.89 \times 10^{-4}$ M	$+3.89 \times 10^{-4}$ M
Eq. conc. M	0.350*	3.89×10^{-4} M	3.89×10^{-4}

* 3.89×10^{-4} M is too small – so it does not have to be subtracted

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

$$K_b = \frac{(3.89 \times 10^{-4}\ \text{M})^2}{0.350\ \text{M}} = 4.53 \times 10^{-7}$$

POLYPROTIC ACIDS

A polyprotic acid has more than one acidic proton—for example, H_2SO_4, H_2SO_3, H_2CO_3, H_3PO_4.

These acids have successive ionization reactions with K_{a1}, K_{a2}, . . .

The calculations of the pH includes ionization of all the protons and then adding all the concentrations to calculate the final pH.

K_a FOR POLYPROTIC ACIDS

Some acid ionization Constants for di and triprotic acids at 25 °C

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Sulfuric acid	H_2SO_4	Very large	1.3×10^{-2}	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-4}	6.1×10^{-5}	
Sulfurous acid	H_2SO_3	1.3×10^{-9}	6.3×10^{-8}	
Ascorbic acid (Vit.C)	$H_2C_6H_6O_6$	8.0×10^{-10}	1.6×10^{-12}	
Carbonic acid	H_2CO_3	4.2×10^{-10}	4.8×10^{-11}	
Hydrosulfuric acid	H_2S	9.5×10^{-14}	1.0×10^{-19}	
Phosphoric acid	H_3PO_4	7.5×10^{-4}	6.2×10^{-8}	4.2×10^{-13}

EXAMPLE 7: POLYPROTIC ACID pH

Tartaric acid, $H_2C_4H_4O_6$, is a diprotic acid used in food products. What is the pH of a **0.10 *M* solution**? What is the concentration of the $C_4H_4O_6^{2-}$ ion in the same solution? $K_{a1} = 9.2 \times 10^{-4}$; $K_{a2} = 4.3 \times 10^{-5}$.

Answer: Find the first and second ionizations…

$$H_2C_4H_4O_{6(aq)} \rightleftharpoons H^+_{(aq)} + HC_4H_4O_6{}^-_{(aq)}$$

Initial	0.10	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	x

$$K_{a_1} = \frac{[H_3O^+]\,[HA^-]}{[H_2A]}$$

$$9.2 \times 10^{-4} = \frac{x^2}{0.10 - x}$$

Check ionization

$$\frac{0.100\ \text{M}}{9.2 \times 10^{-4}} = 108$$ which is just about 100, so cannot ignore x

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EXAMPLE 7: POLYPROTIC ACID CONTD….1

- Use the quadratic equation.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$9.2 \times 10^{-4}(0.10 - x) = x^2$$

$$9.2 \times 10^{-5} - 9.2 \times 10^{-4}x = x^2$$

$$x^2 + 9.2 \times 10^{-4}x - 9.2 \times 10^{-5} = 0$$

$$a = 1 \qquad b = 9.2 \times 10^{-4} \qquad c = -9.2 \times 10^{-5}$$

$$x = \frac{-(9.2 \times 10^{-4}) \pm \sqrt{(9.2 \times 10^{-4})^2 - 4(1)(-9.2 \times 10^{-5})}}{2(1)}$$

$$x = \frac{-(9.2 \times 10^{-4}) \pm (1.92 \times 10^{-2})}{2} = -4.6 \times 10^{-4} \pm 9.6 \times 10^{-3}$$

$$x = 9.1 \times 10^{-3} \quad \text{and} \quad x = -1.0 \times 10^{-2}$$

- At the end of the first acid ionization equilibrium, the concentrations are
  - $[H_3O^+] = 9.1 \times 10^{-3}$ M
  - $[HA^-] = 9.1 \times 10^{-3}$ M
  - $[H_2A] = 9.0 \times 10^{-4}$ M
- Use these to calculate the 2nd conc. of hydronium ion.

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EXAMPLE 7: POLYPROTIC ACID CONTD....2

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	$HC_4H_4O_6^-{}_{(aq)}$	$\rightleftharpoons$	$H^+{}_{(aq)}$ +	$C_4H_4O^{2-}{}_{(aq)}$
Initial	0.0091		0.0091	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.0091 - x$		$0.0091 + x$	x

$$K_{a_2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \qquad 4.3 \times 10^{-5} = \frac{(0.0091 + x)x}{(0.0091 - x)}$$

$$\textit{Check again if we can subtract } x = \frac{.0091}{4.3} = 211, > 100\text{ , so ignore } x$$

- Calculating the final pH. $[C_4H_4O_6^{2-}] = 4.3 \times 10^{-5}\ M$

$$[HC_4H_4O_6^-] = 9.1 \times 10^{-3}\ M$$

Use this for pH → $[H_3O^+] = 9.1 \times 10^{-3}\ M$

$$[H_2C_4H_4O_6] = 9.0 \times 10^{-4}\ M$$

$$pH = -\log\left(9.1 \times 10^{-3}\right) = 2.04$$

KEY CONCEPTS

- Calculation of pH and pOH of weak acids and bases
- Calculation of K_a and K_b of weak acids and bases
- Calculation of pH for diprotic acids.