ACIDS & BASES INTRODUCTION: DEFINITIONS, PH, AND K VALUES

CHEMISTRY 165 // SPRING 2020



What is an acid?

Let's stick with the Brønsted-Lowry definition:

ACID: Proton (H⁺) *donor*, or gives off free H⁺

BASE: Proton (H⁺) *acceptor*, or reacts with H⁺ to give off OH⁻

To help, consider the following examples of acids. Notice how the acids give off H⁺ and an anion.

ACID $HNO_3 \rightarrow H^+ + NO_3^ CH_3COOH \rightleftharpoons H^+ + CH_3COO^ NH_4^+ \rightleftharpoons H^+ + NH_3$ $H_2CO_3 \rightleftharpoons H^+ + HCO_3^ HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $HCI \rightarrow H^+ + CI^-$

In general, we can express the reactivity

of ACIDS and BASES as:

 $HA \rightleftharpoons H^+ + A^-$

What is an acid? What is a base?

Let's stick with the <u>Brønsted-Lowry</u> definition: ACID: Proton (H⁺) *donor*, or gives off free H⁺

BASE: Proton (H⁺) acceptor, or reacts with H⁺ to give off OH⁻

To help, consider the following examples of acids. Notice how the acids give off H⁺ and an anion. Now consider the following examples of bases, some reacting with water (H₂O). Pay close attention to how each base reacts (with water) and what each base gives off.

ACID

$$HNO_{3} \rightarrow H^{+} + NO_{3}^{-}$$

$$CH_{3}COOH \rightleftharpoons H^{+} + CH_{3}CO$$

$$NH_{4}^{+} \rightleftharpoons H^{+} + NH_{3}$$

$$H_{2}CO_{3} \rightleftharpoons H^{+} + HCO_{3}^{-}$$

$$HCO_{3}^{-} \rightleftharpoons H^{+} + CO_{3}^{2-}$$

$$HCI \rightarrow H^{+} + CI^{-}$$

In general, we can express the reactivity

of **ACIDS** and **BASES** as:

 $HA \rightleftharpoons H^+ + A^-$

BASE

 $CN^{-} + H_2O \rightleftharpoons HCN + OH^{-}$ $OO^{-} SO_4^{2-} + H_2O \rightleftharpoons HSO_4^{-} + OH^{-}$ $HSO_4^{-} + H_2O \rightleftharpoons H_2SO_4 + OH^{-}$ $NH_3 + H_2O \rightleftharpoons NH_4^{+} + OH^{-}$ $NaOH \rightarrow Na^{+} + OH^{-}$ $Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^{-}$

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

What is an acid? What is a base?

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ACID: Proton (H⁺) *donor*, or gives off free H⁺

BASE: Proton (H⁺) *acceptor*, or reacts with H⁺ to give off OH⁻

ACID

 $HA \rightleftharpoons H^+ + A^-$

Exercise: Go back to the previous slide and identify the conjugate-bases and conjugate-acids of each of the acids and bases, respectively.

HA: acid A⁻: conjugate-base

$$K_{\rm a} = \frac{[\rm H^+][\rm A^-]}{[\rm HA]}$$

BASE

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

B: base HB⁺: conjugate-acid

Let's come back to this chart in a bit.



Measuring acidity or basicity: pH & pOH

Because Brønsted-Lowry theory defines acids as giving off H⁺ and bases as giving off OH⁻, we can formulate a metric to determine how *acidic* an acid is and how *basic* a base is.

Consider the aqueous equilibria associated with acids and bases below and their equilibrium constants: K_a and K_b . For an acid, the amount of H⁺ liberated, [H⁺], will define its acidity. For a base, the amount of OH^- liberated, $[OH^-]$, will define its basicity.

Because concentrations can span large ranges (from very small to very large), we can take a logarithm of the concentrations to give us a more "user-friendly" number: pH and pOH.

ACID

 $HA \rightleftharpoons H^+ + A^-$

$$K_{\rm a} = \frac{[\rm H^+][\rm A^-]}{[\rm HA]}$$

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

BASE

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

$$K_{\rm b} = \frac{[\rm HB^+][\rm OH^-]}{[\rm B]}$$

 $pOH = -\log[OH^{-}]$

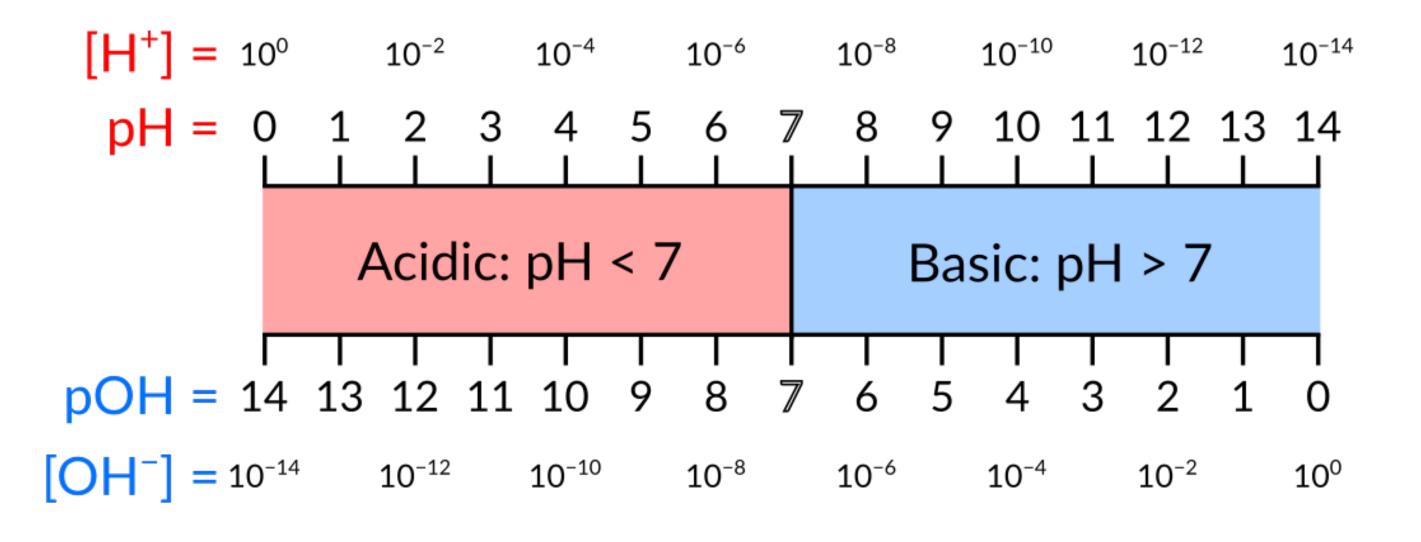
Measuring acidity or basicity: pH & pOH

Typically, we work in terms of pH, where acidic solutions have pH < 7 and basic solutions have pH > 7. Neutral solutions (pure water) have pH = 7.

The pH scale below shows how we can relate $[H^+]$ and pH (or $[OH^-]$ and pOH).

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

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



pH (or $[OH^{-}]$ and pOH). $pOH = -\log[OH^{-}]$

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

pH + pOH = 14

What is does K_a or K_b tell me?

Since the K_a (or K_b) value is	an equilibrium constant, its	ACID	BASE
magnitude tell us to what extent the acid (or base)		$HA \rightleftharpoons H^+ + A^-$	$B + H_2O \rightleftharpoons HB^+ + OH^-$
dissociates to give off H ⁺ (or Therefore, we have the follow		HA: acid A⁻: conjugate base	B: base HB ⁺ : conjugate acid
Strong Acid	Weak Acid	$[H^+][A^-]$	[HB ⁺][OH ⁻]
$K_{\rm a} > 1$	$K_{\rm a} < 1$	$\longleftarrow K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$	$K_{\rm b} = \frac{[\rm HB^+][\rm OH^-]}{[\rm B]}$
Complete dissociation; <u>Not</u> an equilibrium;	Partial dissociation; Equilibrium lies to the left;	$pH = -log[H^+]$ $[H^+] = 10^{-pH}$	$pOH = -log[OH^{-}]$ $[OH^{-}] = 10^{-pOH}$
All H ⁺ and A ⁻ in solution No HA	Mostly HA in solution, some H ⁺ and A ⁻		
$HA \rightarrow H^+ + A^-$	$HA \rightleftharpoons H^+ + A^-$		
	, HBr, HI, H ₂ SO ₄ , HNO ₃ , HClC H, NaOH, KOH, Ca(OH) ₂ , Ba(C		nese strong acids/base! hing else is weak.

Calculate the pH of each of the following solutions of strong and strong bases.

- answer -

	•		
а	ci	C	S
	•		•

	Concentration	Acid/Base	рН
А	0.001 M	HI	
В	0.1 M	H_2SO_4	
С	0.76 M	NaOH	
D	2.8 × 10 ⁻⁴ M	Ca(OH) ₂	

Calculate the pH of each of the following solutions of strong a and strong bases.

- answer -

First, realize that strong acids and strong bases will dissociate completely in solution. Therefore, we can consider unidirectional arrows in place of the equilibrium arrows.

 $HA \rightarrow H^+ + A^-$

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 $BOH \rightarrow B^+ + OH^-$

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 $HA \rightarrow H^+ + A^-$

As such, calculating the pH of solutions A and C is fairly straightforward. Solution A: $HI \rightarrow H^+ + I^-$ Solution C: NaOH \rightarrow Na⁺ + OH⁻

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As such, calculating the pH of solutions A and C is fairly straightforward.

Solution A: HI
$$\rightarrow$$
 H⁺ + I⁻
[H⁺] = $\frac{0.001 \text{ mol HI}}{1 \text{ L}} \times \frac{1 \text{ mol H}^+}{1 \text{ mol HI}} = 0.001 \text{ M}$
pH = $-\log(0.001) = 3.0$

acids		Concentration	Acid/Base	pН
	А	0.001 M	HI	
	В	0.1 M	H_2SO_4	
	С	0.76 M	NaOH	
	D	2.8 × 10 ⁻⁴ M	Ca(OH) ₂	

 $BOH \rightarrow B^+ + OH^-$

Solution C: NaOH \rightarrow Na⁺ + OH⁻ $[OH^{-}] = \frac{0.76 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol OH}^{-}}{1 \text{ mol NaOH}} = 0.76 \text{ M}$ $pOH = -\log(0.76) = 0.11_9$ pH = 14 - pOH = 13.88

Calculate the pH of each of the following solutions of strong a and strong bases.

- answer -

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pH = $-\log(0.001) = 3.0$

For solutions B and C, we need to take into account the stoichiometry of the dissociation. Solution B: $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

acids		Concentration	Acid/Base	pН
	А	0.001 M	HI	
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Solution D: Ca(OH)₂ \rightarrow Ca²⁺ + 2OH⁻

Calculate the pH of each of the following solutions of strong a and strong bases.

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As such, calculating the pH of solutions A and C is fairly straightforward.

Solution A: HI
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[H⁺] = $\frac{0.001 \text{ mol HI}}{1 \text{ L}} \times \frac{1 \text{ mol H}^+}{1 \text{ mol HI}} = 0.001 \text{ M}$
pH = $-\log(0.001) = 3.0$

For solutions B and C, we need to take into account the stoichiometry of the dissociation.

Solution B:
$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

 $[H^+] = \frac{0.1 \mod H_2SO_4}{1 L} \times \frac{2 \mod H^+}{1 \mod H_2SO_4} = 0.2 M$
 $pH = -\log(0.2) = 0.7$

acids		Concentration	Acid/Base	pН
	А	0.001 M	HI	
	В	0.1 M	H_2SO_4	
	С	0.76 M	NaOH	
	D	2.8 × 10 ⁻⁴ M	Ca(OH) ₂	

 $BOH \rightarrow B^+ + OH^-$

Solution C: NaOH \rightarrow Na⁺ + OH⁻ $[OH^{-}] = \frac{0.76 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol OH}^{-}}{1 \text{ mol NaOH}} = 0.76 \text{ M}$ $pOH = -\log(0.76) = 0.11_9$ pH = 14 - pOH = 13.88

Solution D: Ca(OH)₂ \rightarrow Ca²⁺ + 2OH⁻ $[OH^{-}] = \frac{2.8 \times 10^{-4} \text{ mol Ca}(OH)_2}{1 \text{ L}} \times \frac{2 \text{ mol OH}^{-}}{1 \text{ mol Ca}(OH)_2} = 5.6 \times 10^{-4} \text{ M}$ $pOH = -\log(5.6 \times 10^{-4}) = 3.25_2$ pH = 14 - pOH = 10.75

Calculate the pH of a 100.00 mL solution of 0.10 M acetic acid (CH₃COOH) where $K_a = 1.76 \times 10^{-5}$ at 25 °C.

- answer -

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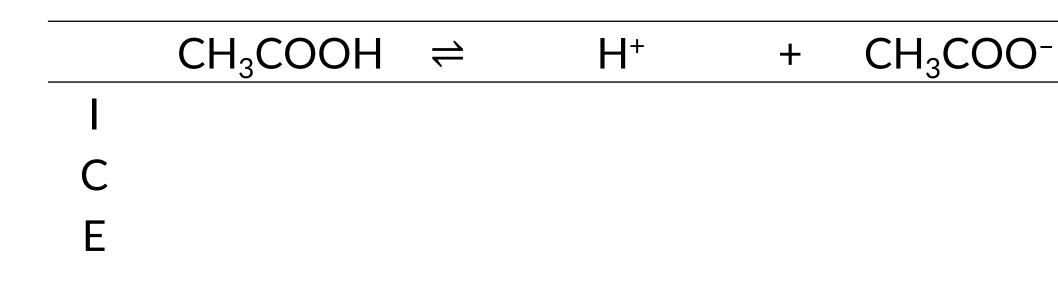
- answer -

First, note that CH_3COOH is a weak acid because K_a is small. Therefore, we have to consider the equilibrium process. Always being by writing out the balanced equilibrium expression for the weak acid dissociation.

CH₃COO⁻ $CH_3COOH \rightleftharpoons$ H^+ +

Calculate the pH of a 100.00 mL solution of 0.10 M acetic acid (CH₃COOH) where $K_a = 1.76 \times 10^{-5}$ at 25 °C. - answer -

First, note that CH_3COOH is a weak acid because K_a is small. Therefore, we have to consider the equilibrium process. Always being by writing out the balanced equilibrium expression for the weak acid dissociation. Then, write out the equilibrium constant expression based on the Law of Mass Action. Construct an ICE chart.



$$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]} = 1.76 \times 10^{-5}$$

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	CH₃COOH ≓	H+	+	CH ₃ COO⁻
I	0.10 M	0		0
С				
Е				

$$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]} = 1.76 \times 10^{-5}$$

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	CH ₃ COOH	\rightleftharpoons	H+	+	CH₃COO⁻
Ι	0.10 M		0		0
С	- X		+ x		+ x
Е					

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	CH ₃ COOH	; ;	H+	+	CH ₃ COO ⁻
I	0.10 M		0		0
С	- x		+ x		+ X
Е	0.10 – x		X		X

$$K_{\rm a} = \frac{[{\rm H}^+][{\rm CH}_3{\rm COO}^-]}{[{\rm CH}_3{\rm COOH}]} = 1.76 \times 10^{-5}$$

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We can use the equilibrium concentration values to plug into our expression for K_a .

	CH₃COOH ≓	H+	+	CH ₃ COO⁻
I	0.10 M	0		0
С	- x	+ x		+ x
Е	0.10 – x	Х		X

$$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]} = 1.76 \times 10^{-5}$$
$$1.76 \times 10^{-5} = \frac{(x)(x)}{0.10 - x}$$

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We can use the equilibrium concentration values to plug into our expression for K_{a} . Finally solve for x and calculate the pH.

	CH₃COOH ≓	H+ +	CH ₃ COO ⁻
I	0.10 M	0	0
С	- x	+ x	+ x
Е	0.10 – x	X	X

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	CH ₃ COOH	 	H+	+	CH ₃ COO
Ι	0.10 M		0		0
С	- X		+ x		+ x
Е	0.10 – x		X		X

Because the value of K_a is very small, we know that the syst undergo very little change (x value) toward the right in o achieve equilibrium. In other words, we can take "x" to small/negligible and invoke the approximation that: $0.10 - x \approx 0.10$

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$$1.76 \times 10^{-5} = \frac{(x)(x)}{0.10 - x}$$
tem will
order to be very
$$1.76 \times 10^{-5} = \frac{x^{2}}{0.10}$$

$$x = 0.0013_{3} M = [H^{+}]$$

$$pH = -\log(0.0013_{3}) = 2.88$$

Calculate the pH of a solution that is 0.20 M NH_4^+ if $K_b(NH_3) = 1.8 \times 10^{-5}$ at 25 °C.

- answer -

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First, note that NH_4^+ is an acid whose conjugate-base is NH_3 . Since we are given the K_b of the NH_3 , we can extract the value of K_a .

$$K_{\rm w} = K_a \times K_b = 1.0 \times 10^{-14}$$
$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5_6 \times 10^{-10}$$



Calculate the pH of a solution that is 0.20 M NH₄⁺ if $K_{\rm b}(\rm NH_3) = 1.8 \times 10^{-5}$ at 25 °C.

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Now we can see that NH_4^+ is a weak acid and we need to consider the weak acid equilibrium. So, write out the balanced equilibrium expression and the equilibrium constant expression for the weak acid dissociation.

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

$$K_{\rm a} = \frac{[{\rm H}^+][{\rm NH}_3]}{[{\rm NH}_4^+]} = 5.5_6 \times 10^{-10}$$



Calculate the pH of a solution that is 0.20 M NH₄⁺ if $K_{\rm b}(\rm NH_3) = 1.8 \times 10^{-5}$ at 25 °C.

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First, note that NH₄⁺ is an acid whose conjugate-base is NH₃. Since we are given the K_b of the NH₃, we can extract the value of K_a .

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	NH_4^+	4	H+	Ŧ	NH_3
I	0.20		0		0
С	- X		+ x		+ X
Е	0.20 – x		Х		Х

Construct an ICE chart. Fill in the initial values, then the stoichiometric changes, and finally the equilibrium concentration values.

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С	- X		+ x		+ X
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Construct an ICE chart. Fill in the initial values, then the stoichiometric changes, and finally the equilibrium concentration values.

$$K_{a} = \frac{[H^{+}][NH_{3}]}{[NH_{4}^{+}]} = 5.5_{6} \times 10^{-10}$$
$$5.5_{6} \times 10^{-10} = \frac{(x)(x)}{0.20 - x}$$



Calculate the pH of a solution that is 0.20 M NH₄⁺ if $K_{\rm b}(\rm NH_3) = 1.8 \times 10^{-5}$ at 25 °C.

- answer -

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С	- x		+ x		+ x
Е	0.20 – x		X		X

Because the value of K_a is very small, we know that the system will undergo very little change (x value) toward the right in order to achieve equilibrium. In other words, we can take "x" to be very small/negligible and invoke the approximation that:

 $0.20 - x \approx 0.20$

Construct an ICE chart. Fill in the initial values, then the stoichiometric changes, and finally the equilibrium concentration values. We can use the equilibrium concentration values to plug into our expression for K_a . Finally solve for x and calculate the pH.

$$K_{\rm a} = \frac{[{\rm H}^+][{\rm NH}_3]}{[{\rm NH}_4^+]} = 5.5_6 \times 10^{-10}$$

$$5.5_6 \times 10^{-10} = \frac{(x)(x)}{0.20 - x}$$

ill
o
y
$$5.5_6 \times 10^{-10} = \frac{x^2}{0.20}$$
$$x = 1.0_5 \times 10^{-5} \text{ M} = [\text{H}^+]$$
$$p\text{H} = -\log(1.0_5 \times 10^{-5}) = 4.98$$



Determine the K_a of a 0.0516 M solution of HNO₂ with a pH = 2.34.

- answer -

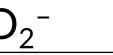
Determine the K_a of a 0.0516 M solution of HNO₂ with a pH = 2.34.

- answer -

HNO₂ is a weak acid, so we can start by writing the weak acid dissociation equilibrium and the associated equilibrium expression.

HNO ₂	 	H+	+	NO
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$$K_{\rm a} = \frac{[\rm H^+][\rm NO_2^-]}{[\rm HNO_2]}$$





Determine the K_a of a 0.0516 M solution of HNO₂ with a pH = 2.34.

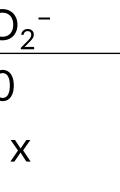
- answer -

 HNO_2 is a weak acid, so we can start by writing the weak acid dissociation equilibrium and the associated equilibrium expression.

Again, we can construct an ICE chart. Fill in the initial values, then the stoichiometric changes, and finally the equilibrium concentration values. Now what?

	HNO ₂	+	H+	+	NO
I	0.0516		0		0
С	- X		+ x		+ ;
Е	0.0516 – x		X		Х

$$K_{a} = \frac{[H^{+}][NO_{2}^{-}]}{[HNO_{2}]}$$
$$= \frac{(x)(x)}{0.0516 - x}$$





Determine the K_a of a 0.0516 M solution of HNO₂ with a pH = 2.34. - answer -

 HNO_2 is a weak acid, so we can start by writing the weak acid dissociation equilibrium and the associated equilibrium expression.

Again, we can construct an ICE chart. Fill in the initial values, then the stoichiometric changes, and finally the equilibrium concentration values. Now what?

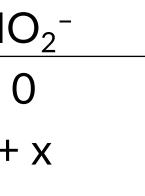
They give us the pH, which tells us $[H^+]$ at equilibrium, and remember that $x = [H^+]$.

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

[H⁺] = $10^{-pH} = 10^{-2.34} = 0.0045_7 M$

	HNO_2	\rightleftharpoons	H+	+	NO
I	0.0516		0		0
С	- x		+ x		+)
Е	0.0516 – x		Х		Х

$$K_{a} = \frac{[H^{+}][NO_{2}^{-}]}{[HNO_{2}]}$$
$$= \frac{(x)(x)}{0.0516 - x}$$





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They give us the pH, which tells us $[H^+]$ at equilibrium, and remember that $x = [H^+]$. Let's replace this value into the ICE chart.

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

 $[H^+] = 10^{-pH} = 10^{-2.34} = 0.0045_7 M$

	HNO ₂	_	H+	+	
I	0.0516		0		
С	- 0.0045 ₇		+ 0.00457		+
Е	0.0516 - 0.0045 ₇		0.0045 ₇		(

$$K_{a} = \frac{[H^{+}][NO_{2}^{-}]}{[HNO_{2}]}$$
$$= \frac{(x)(x)}{0.0516 - x}$$

 NO_2^- 0.00457 0.00457



Determine the K_a of a 0.0516 M solution of HNO₂ with a pH = 2.34. - answer -

HNO₂ is a weak acid, so we can start by writing the weak acid dissociation equilibrium and the associated equilibrium expression.

Again, we can construct an ICE chart. Fill in the initial values, then the stoichiometric changes, and finally the equilibrium concentration values. Now what?

They give us the pH, which tells us $[H^+]$ at equilibrium, and remember that $x = [H^+]$. Let's replace this value into the ICE chart. Finally, solve for K_a from the equilibrium concentrations.

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

 $[H^+] = 10^{-pH} = 10^{-2.34} = 0.0045_7 M$

	HNO ₂	/	H+	+	
I	0.0516		0		
С	- 0.0045 ₇		+ 0.00457		+
Е	0.0516 - 0.0045 ₇		0.0045 ₇		(

$$K_{a} = \frac{[H^{+}][NO_{2}^{-}]}{[HNO_{2}]}$$
$$= \frac{(x)(x)}{0.0516 - x}$$
$$= \frac{(0.0045_{7})^{2}}{0.0516 - 0.0045_{7}}$$
$$K_{a} = 4.5 \times 10^{-4}$$

 NO_2^- - 0.0045₇ 0.00457

