

Example: Calculate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in pure water at 0°C , 25°C and 100°C .

t	K_w
0°C	1.14×10^{-15}
10°C	2.97×10^{-15}
20°C	6.88×10^{-15}
25°C	1.01×10^{-14}
30°C	1.46×10^{-14}
40°C	2.88×10^{-14}
50°C	5.31×10^{-14}
100°C	5.45×10^{-13}

Digging deeper: The correct definition of pH

If you were to use a pH electrode for measuring pH, you would find that the pH of 0.01 mol L⁻¹ HCl(aq) is 2.04 (not 2.00)!! Even more dramatically, the pH of 7.6 mol L⁻¹ HCl(aq) is about -1.85 (not -0.88)!! How can this be?

The response of a pH electrode is most directly a measure of the “activity” of the H⁺ ion in the solution, not a measure of [H⁺]. The activity of the H⁺ ion, a_{H⁺}, is sometimes referred to as an “effective” concentration that is usually related to the true concentration, [H⁺], as follows:

$$a_{\text{H}^+} = \gamma [\text{H}^+]$$

The activity coefficient, γ , takes into account various interactions occurring amongst ions and molecules in solution. Ions interact strongly with each other, over long distances, and with solvent molecules. Consequently, ions in solution can have a pronounced affect on the behaviour, and activities, of dissolved ions.

For very dilute solutions, the value of γ will be close to “1”. Experiment shows that the activity of H⁺ is close to the concentration of H⁺ if the concentrations of all species are 0.001 mol L⁻¹ or less, but for most solutions the activity of H⁺ is significantly different than [H⁺].

The correct definition for pH is as follows:

$$\text{pH} \equiv -\log_{10} a_{\text{H}^+}.$$

The definition of pH we use in this course is an approximate one and it would be more appropriate to write $\text{pH} \approx -\log_{10}[\text{H}^+]$. The following data illustrate that there can be significant error if we use the approximate equation for pH.

	$\text{pH} \approx -\log_{10}[\text{H}^+]$	True pH
25 mL of 0.015 mol L ⁻¹ HCl(aq)	1.85	1.79
25 mL of 0.015 mol L ⁻¹ HCl(aq) plus 22 mL of 5 mol L ⁻¹ CaCl ₂ (aq)	2.10	0.91

The differences in results arise because of the presence of other ions in the solution (Cl⁻ and Ca²⁺) which interact with H⁺ and affect the activity of H⁺ in solution. It is especially interesting to compare the pH's before and after dilution of HCl(aq) with CaCl₂(aq). If we were to use the approximate definition for pH, we would mistakenly conclude that the pH of the solution increases upon dilution when in reality, the pH decreases! It is true the dilution of HCl(aq) with CaCl₂(aq) causes a decrease in [H⁺], but the observed decrease in pH shows that a_{H⁺} increases. In this particular instance, the addition of Ca²⁺ and Cl⁻ ions leads ultimately an increase in the activity of H⁺, even though [H⁺] decreases.

Are you responsible for remembering all of this? No. We will use the equation $\text{pH} \approx -\log_{10}[\text{H}^+]$ but you please remember that this an approximate equation for pH.

The value of the activity coefficient, γ , depends on various solution properties but especially on the so-called ionic strength, I , of the solution:

$$I = \sum_i z_i^2 C_i .$$

In the equation above, z_i is the charge on a particular ion in solution and C_i is the concentration of that ion in the solution. The ionic strength depends on the charges and concentrations of all of the different types of ions in solution.

K_a and K_b values for weak acids and weak bases are extensively tabulated. A selection of values is given in the table below.

K_a and K_b for some Acids and Bases	
Acid	K_a
Acetic, CH_3COOH	1.8×10^{-5}
Aluminum ion, $\text{Al}(\text{H}_2\text{O})^{3+}$	1.4×10^{-5}
Ascorbic, $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.9×10^{-5} (K_{a1})
$\text{HC}_6\text{H}_6\text{O}_6^-$	1.6×10^{-12} (K_{a2})
Benzoic, $\text{HC}_7\text{H}_5\text{O}_2$	6.3×10^{-5}
Carbonic, H_2CO_3	4.4×10^{-7} (K_{a1})
HCO_3^-	4.7×10^{-11} (K_{a2})
Chloroacetic, CH_2ClCOOH	1.41×10^{-3}
Formic, HCOOH	1.8×10^{-4}
Hypobromous, HOBr	2.06×10^{-9}
Hypochlorous, HOCl	2.9×10^{-8}
Hydrofluoric, HF	6.6×10^{-4}
Hydrogen sulfide, H_2S	1.0×10^{-7} (K_{a1})
HS^-	1.0×10^{-19} (K_{a2})
Iron (III) ion, $\text{Fe}(\text{H}_2\text{O})^{3+}$	7.9×10^{-3}
Nitrous, HNO_2	7.2×10^{-4}
Phosphoric, H_3PO_4	7.1×10^{-3} (K_{a1})
H_2PO_4^-	6.3×10^{-8} (K_{a2})
HPO_4^{2-}	4.2×10^{-13} (K_{a3})
Sulfuric, H_2SO_4	strong
HSO_4^-	1.1×10^{-2} (K_{a2})
Oxalic, $\text{H}_2\text{C}_2\text{O}_4$	5.9×10^{-2} (K_{a1})
HC_2O_4^-	6.40×10^{-5} (K_{a2})
Hydrazoic, HN_3	1.9×10^{-5}
Hydrocyanic, HCN	6.2×10^{-10}
Phenol, $\text{C}_6\text{H}_5\text{OH}$	1.0×10^{-10}
Base	K_b
Ammonia, NH_3	1.8×10^{-5}
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	7.4×10^{-10}
Trimethylamine $\text{N}(\text{CH}_3)_3$	6.3×10^{-5}
Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$	4.3×10^{-4}
Diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$	6.9×10^{-4}
Pyridine, $\text{C}_5\text{H}_5\text{N}$	1.5×10^{-9}
Morphine, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$	8.0×10^{-7}

What is a weak acid?

If $K_a \times C_0 \leq 10^{-16}$, then the acid strength and/or concentration of acid is/are too small to have any effect on the pH of the solution (i.e. pH = 7.00 at 25°C).

Similarly, if $K_b \times C_0 \leq 10^{-16}$, then the base strength and/or concentration is/are too small to have any effect on the pH of the solution (i.e. pH = 7.00 at 25°C).

As an example, consider *t*-butyl alcohol, $(\text{CH}_3)_3\text{COH}$, for which $K_a = 1 \times 10^{-19}$. In 1.0 mol L^{-1} $(\text{CH}_3)_3\text{COH}(\text{aq})$, the concentration of $(\text{CH}_3)_3\text{CO}^-$ is only $1.0 \times 10^{-13} \text{ mol L}^{-1}$ and the pH of the solution is 7.00. It is not appropriate to say that $(\text{CH}_3)_3\text{COH}$ is a weak acid. Its acid strength is too small to affect pH.

For practical purposes:

- a weak acid has K_a less than 1 but larger than 10^{-14} .
- a weak base has K_b less than 1 but larger than 10^{-14} .

If K_a (or K_b) is less than 10^{-16} , then the acid (or base) is too weak to affect the pH of the solution.

Tip: If you are asked to calculate the pH of a solution, then ask yourself: Is the dissolved substance a strong acid or a strong base? If the substance is not a strong acid or strong base, then you will have to consult a table of ionization constants to find the K_a or K_b value.

Remember!
We expect you to memorize the lists of strong acids and bases.

Example:

Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$ and the pH for $0.125 \text{ mol L}^{-1} \text{ HBr(aq)}$

Example:

Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$ and the pH for $0.0125 \text{ mol L}^{-1} \text{ Ba(OH)}_2(\text{aq})$

The solubility of Ca(OH)_2 in water is about 0.01 mol L^{-1} . That of Ba(OH)_2 is about 0.04 mol L^{-1} .

Example:

Calculate $[\text{CH}_3\text{COOH}]$, $[\text{CH}_3\text{COO}^-]$, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$ at equilibrium when 0.125 mol CH_3COOH is dissolved in water to make 1.0 L of solution at 25°C . What is the pH? What is the percent ionization of CH_3COOH ?

When a weak acid (or a weak base) is dissolved in water, only some of the molecules react with water molecules. In order to calculate the pH of the solution, we must set up and solve an equilibrium problem.

Example: Calculate $[\text{CH}_3\text{CH}_2\text{NH}_2]$, $[\text{CH}_3\text{CH}_2\text{NH}_3^+]$, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$ at equilibrium when 0.0117 mol $\text{CH}_3\text{CH}_2\text{NH}_2$ is dissolved in water to make 1.0 L of solution at 25°C . What is the pH? What is the percent ionization of $\text{CH}_3\text{CH}_2\text{NH}_2$?

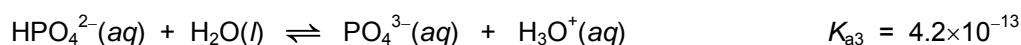
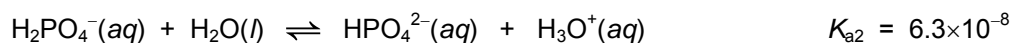
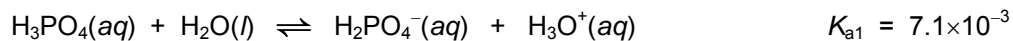
Example: Given that $K_{a1} = 5.4 \times 10^{-2}$ and $K_{a2} = 5.3 \times 10^{-5}$ at 25°C for $\text{H}_2\text{C}_2\text{O}_4$, calculate the pH of $0.10 \text{ mol L}^{-1} \text{H}_2\text{C}_2\text{O}_4(\text{aq})$. Estimate the equilibrium concentration of $\text{C}_2\text{O}_4^{2-}$.

For most polyprotic acids, we normally do not have to consider the second or third ionization steps when calculating the pH. An important exception, however, is H_2SO_4 . You might recall that sulfuric acid, H_2SO_4 , is a strong acid (i.e. the first ionization step goes to completion and generates a significant amount of HSO_4^- that can ionize further). To calculate the pH of an aqueous solution of H_2SO_4 , we must also consider the contribution made by second ionization step for which $K_{a2} = 1.1 \times 10^{-2}$.

Example: Calculate the pH of $0.10 \text{ mol L}^{-1} \text{H}_2\text{SO}_4(aq)$.

Systematic treatment of equilibrium

For a polyprotic acid, such as H_3PO_4 , there are several equilibrium processes to consider and each one has its own equilibrium constant. If we wanted to calculate the pH of $0.10 \text{ mol L}^{-1} \text{H}_3\text{PO}_4(\text{aq})$ without making any simplifying approximations, we must write down all of the relevant equilibrium expressions:



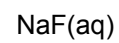
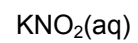
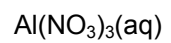
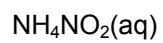
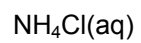
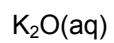
The equilibrium constant expressions give us four equations involving six unknown concentrations: $[\text{H}_3\text{PO}_4]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{HPO}_4^{2-}]$, $[\text{PO}_4^{3-}]$, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$.

Example: What are the mass and charge balance equations for $0.10 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4(\text{aq})$?

Example: Write down the mass and charge balance equations for $1.0 \times 10^{-8} \text{ mol L}^{-1} \text{ HCl}(aq)$. Estimate the pH of this solution.

The "simple-minded" approach to this problem would be to say that since all of the HCl ionizes (which is true), then $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-8} \text{ mol L}^{-1}$ and $\text{pH} = 8.0$. Obviously, this result is nonsense since dissolving strong acid in water will never give us a basic solution!

Example: Without doing any pH calculations, arrange the following solutions in order of increasing pH. Assume that each solution is prepared by dissolving 1.0 mol of the salt in water to give 1.0 L of solution at 25°C



Example: Calculate the pH of $0.10 \text{ mol L}^{-1} \text{ NaF}(aq)$.

Example: Calculate the pH of $0.10 \text{ mol L}^{-1} \text{ NH}_4\text{NO}_3(\text{aq})$.

Example: Is an aqueous solution NaHCO_3 acidic, basic or neutral? What about $\text{NaHSO}_4(\text{aq})$? What about $\text{Na}_2\text{C}_2\text{O}_4(\text{aq})$?

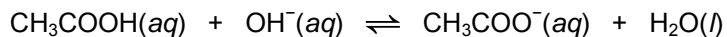
Example: Calculate the percent ionization of CH_3COOH in each of the following solutions.

(a) 1.0 L of $0.125 \text{ mol L}^{-1} \text{CH}_3\text{COOH}(\text{aq})$

(b) 1.0 L of a solution that contains $0.125 \text{ mol CH}_3\text{COOH}$ and $0.025 \text{ mol CH}_3\text{COONa}$

Example: A solution is prepared by mixing 0.0150 mol CH_3COOH and 0.0050 mol NaOH in water to make 1.0-L of solution at 298 K. What is the pH of the final solution?

┌ **Aside:** For the previous example, you can obtain the same result using another approach. Since $K_{\text{neutr}} = K_a^{\text{HA}} / K_w = 1.8 \times 10^9 \gg 1$, we can assume that the reaction between CH_3COOH and NaOH goes 100% to completion but then backs up a little to establish a true equilibrium state.



mix:	0.0150 mol/L	0.0050 mol/L	
assuming 100%:	0.0100	0	0.0050 mol/L
backing up:	+ x	+ x	- x
equilibrium:	0.0100+x	x	0.0050 - x

At equilibrium, we must have:

$$K_{\text{neutr}} = \frac{(0.0050 - x)}{(0.0100 + x)(x)} \approx \frac{(0.0050)}{(0.0100)(x)} \Rightarrow x \approx \frac{(0.0050)}{(0.0100)(K_{\text{neutr}})} = 2.78 \times 10^{-10}$$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (2.78 \times 10^{-10}) = 3.6 \times 10^{-5} \Rightarrow \text{pH} = 4.44 \quad \lrcorner$$

Example: Which of the following combinations produces a buffer solution when the substances are dissolved together in water to make 1.0 L of solution?

(i) 0.700 mol CH_3COOH + 0.400 mol CH_3COONa

(ii) 1.00 mol CH_3COOH + 0.60 mol NaOH

(iii) 0.10 mol NH_3 + 0.15 mol NH_4Cl

(iv) 0.10 mol HCl + 0.10 mol NaCl

Example: A buffer solution is prepared by dissolving 0.125 mol CH_3COOH and 0.025 mol CH_3COONa in water to make 1.0 L of solution at 25°C . What is the pH of this solution?

Example: (Preparation of a buffer solution)

- (a) Calculate the amount of CH_3COONa that must be added to 0.500 L of $1.0 \text{ mol L}^{-1} \text{CH}_3\text{COOH}(aq)$ to obtain a buffer with $\text{pH} = 5.00$.
- (b) Calculate the amount of NaOH that must be added to 0.500 L of $1.0 \text{ mol L}^{-1} \text{CH}_3\text{COOH}(aq)$ to obtain a buffer with $\text{pH} = 5.00$.

This example shows that a buffer of desired pH can be prepared **directly** (e.g. mixing the appropriate amounts of HA and NaA together in water), or **indirectly** (e.g. mixing HA with an appropriate amount of NaOH).

Buffer Action (and Buffer Capacity)

A buffer solution converts strong acid into weak acid and strong base into weak base. If the addition of strong acid (or strong base) does not change the "buffer ratio" appreciably, then the pH of the buffer does not change much.

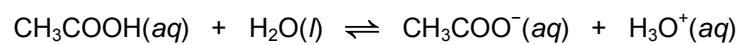
The buffer capacity of a solution is defined as the number of moles of strong base that must be added to 1.0 L of solution to raise the pH by one unit.

Example: Calculate the final pH of the solution when 5.0×10^{-3} mol NaOH is added to (a) 1.0-L of pure water at 25.0°C ; (b) 1.0-L of a buffer containing 0.125 mol CH_3COOH and 0.025 mol CH_3COONa .

Example: A 50.0-mL sample of $0.10 \text{ mol L}^{-1} \text{ CH}_3\text{COOH(aq)}$ is titrated with $0.20 \text{ mol L}^{-1} \text{ NaOH(aq)}$. Calculate the pH at each of the following points.

- (a) before the titration starts
- (b) after adding 5.0 mL of NaOH(aq)
- (c) after adding 10.0 mL of NaOH(aq)
- (d) at the equivalence point
- (e) 10.0 mL past the equivalence point

Example: When it is appropriate to set up and use the following equilibrium to calculate the pH of the solution?



Example: When it is appropriate to set up and use the following equilibrium to calculate the pH of the solution?

