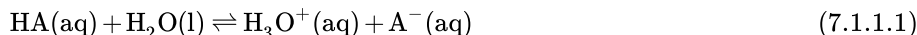
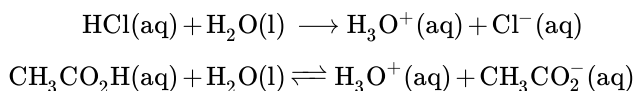


7.1.1: Arrhenius Model

The Arrhenius acid-base concept defines acids and bases in terms of how they affect the amount of hydronium ions, H_3O^+ , (and by extension hydroxide ions, OH^-) in aqueous solutions. Simply, in the Arrhenius definition an acid is a substance that increases the concentration of hydronium ions when it is dissolved in water. This typically occurs when the acid dissociates by loss of a proton to water according to the general equation:



where A is the deprotonated form of the acid. For example, what hydrochloric and acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, have in common is that both increase the amount of hydronium ion when they are dissociated in solution.



In terms of the Arrhenius definition, the major difference between hydrochloric and acetic acid is that hydrochloric acid dissociates completely in solution to yield stoichiometric amounts of H_3O^+ , while acetic acid only partially dissociates. Acids like HCl that completely dissociate in water are classified as strong in the Arrhenius definition, while those like acetic acid that do not are classified as weak.

Although all weak acids incompletely dissociate, the extent of dissociation can vary widely. The relative strengths of weak Arrhenius acids is conveniently expressed in terms of the equilibrium constant for their acid dissociation reaction, K_a .

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The $\text{p}K_a$ values for selected weak acids are given in Table 7.1.1.1

Table 7.1.1.1: Values of K_a , $\text{p}K_a$, K_b , and $\text{p}K_b$ for selected monoprotic acids.

Acid	HA	K_a	$\text{p}K_a$	A^-	K_b	$\text{p}K_b$
sulfuric acid (2nd ionization)	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	NO_2^-	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2^-	5.6×10^{-11}	10.25
benzoic acid	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	6.3×10^{-5}	4.20	$\text{C}_6\text{H}_5\text{CO}_2^-$	1.6×10^{-10}	9.80
acetic acid	$\text{CH}_3\text{CO}_2\text{H}$	1.7×10^{-5}	4.76	CH_3CO_2^-	5.8×10^{-10}	9.24
pyridinium ion	$\text{C}_5\text{H}_5\text{NH}^+$	5.9×10^{-6}	5.23	$\text{C}_5\text{H}_5\text{N}$	1.7×10^{-9}	8.77
hypochlorous acid	HOCl	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	-12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	-21.0

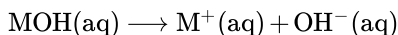
*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

As can be seen from the table the K_a values for weak acids are less than one (otherwise they would not be weak) and vary over many orders of magnitude. Consequently it is customary to tabulate acid ionization constants as $\text{p}K_a$ values:

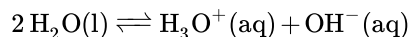
$$\text{p}K_a = -\log K_a$$

Because pK_a values essentially place the K_a values on a negative base ten logarithmic scale, the stronger the weak acid, the lower its pK_a . Weak acids with larger K_a values will have lower pK_a values than weaker acids with smaller K_a . Moreover, each unit increase or decrease in the pK_a corresponds to a tenfold increase or decrease in the corresponding K_a .

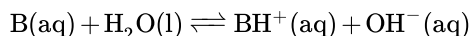
While Arrhenius acids increase the concentration of H_3O^+ in aqueous solution, Arrhenius bases decrease H_3O^+ . Strong bases do this stoichiometrically. Most are hydroxide salts of alkali metals or quaternary ammonium salts that dissociate completely when dissolved in water:



This added hydroxide decreases the concentration of H_3O^+ by shifting the water autoionization equilibrium towards water.



In contrast, most weak bases react with water to produce an equilibrium concentration of hydroxide ion according to the base dissociation reaction



in which B is the weak base. The ionization constant for this reaction, called the **base ionization constant** or K_b , is typically used as a measure of a weak base's strength.

Because both hydroxide and hydronium ion are products of water autoionization, the concentrations of hydronium ion and hydroxide ion in aqueous solution will vary reciprocally with one another. This means that Arrhenius acids can be recognized as substances that decrease the hydroxide concentration and Arrhenius bases as substances that increase it.

Since the Arrhenius acid-base concept is concerned about the state of the water autoionization reaction, Arrhenius acids and bases may also be recognized by their effect on the solution pH. Arrhenius acids decrease the pH and Arrhenius bases will increase it.

NOTE

To qualify as an Arrhenius acid, upon the introduction to water, the chemical must cause, either directly or otherwise:

- an increase in the aqueous hydronium concentration,
- a decrease in the aqueous hydroxide concentration, or
- a decrease in the solution pH.

Conversely, to qualify as an Arrhenius base, upon the introduction to water, the chemical must cause, either directly or otherwise:

- a decrease in the aqueous hydronium concentration,
- an increase in the aqueous hydroxide concentration, or
- an increase in the solution pH.

Because the Arrhenius acid-base model defines acids and bases in terms of their impact on the state of an aqueous solution the Arrhenius concept is unable to describe reactions in nonaqueous solvents, gases, molten liquids, and the solid state. Consequently other models should be used to describe reactions involving the transfer of H^+ and other fragments in nonaqueous media.

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