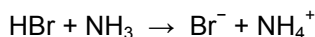


3. Acids and Bases

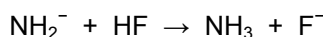
3.1 Brønsted-Lowry Theory

According to the Brønsted-Lowry definition of acids and bases, an acid reacts with a base by exchanging an H^+ . For example,



Here, HBr is the H^+ donor – the acid – while NH_3 is the H^+ acceptor – the base. The H^+ is able to leave the acid because the H-Br bond is polarized – the bonding electrons are shifted towards the bromine atom. The Lewis definition of acids and bases explains that NH_3 is able to accept the H^+ because there is a lone pair of electrons on the nitrogen atom. These electrons are shared to become the fourth N-H bond in NH_4^+ .

Example 3.1: Identify the acid and base in the following reaction:

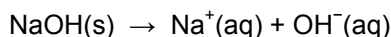


Approach: Look for the reactant that gained an H^+ , and that which lost an H^+ .

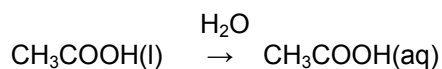
The HF loses an H^+ . It is the H^+ donor – i.e., it is the acid. NH_2^- accepts the H^+ . It is the base. Note that an acid always has an H bonded to an electronegative atom (N, O, F, S, Cl, Br or I – often it is O). A base must have a lone pair of electrons to accept the H^+ . The lone pair is usually on an N atom (often seen for uncharged basic molecules) or an O atom (mostly seen for anionic bases).

Acids and bases form acidic and basic aqueous solutions. Acids and bases can be molecules or ions.

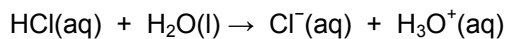
Salts form aqueous solutions by splitting into positive and negative ions that are solvated by water. For example,



Molecular compounds form aqueous solutions by becoming solvated by water. For example, acetic acid (vinegar) dissolves in water according to

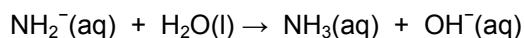


Acids and bases react with water when in aqueous solution. Acids react by donating H^+ to water. For example,



In this reaction, H_2O acts as a base. It accepts an H^+ .

Bases react by accepting an H^+ from water. For example,

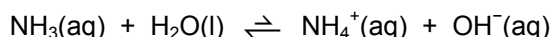


Here, H_2O acts as an acid. It donates an H^+ . Some substances, such as water, can behave as either acids or bases depending on what they react with. They are called *amphoteric*.

3.2 Strong and Weak Acids and Bases

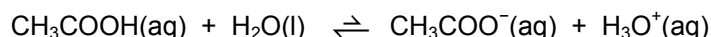
All the chemical reactions shown above have arrows to the right indicating the reaction proceeds to completion. In reality, no reaction proceeds to completion; there is always a reverse reaction that returns products back to reactants. However, we frequently encounter reactions that essentially go to completion. All the reactions listed above are of this type. In such cases, the rate of the reverse reaction is very much smaller than the rate of forward reaction. When equilibrium is obtained – i.e., when the rate of reverse reaction equals the rate of forward reaction – there is very little reactant left. This amount is often negligible. However, there are also many reactions where the rate of reverse reaction is not negligible; in these cases there is a significant amount of “reactant” present at equilibrium.

Many acids and bases react with water only to a limited extent. For example, ammonia only reacts to a limited extent:

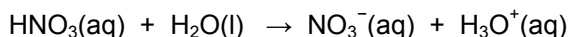


The limited degree of reaction is indicated here by the double arrow (showing forward and reverse reactions). In fact, in an aqueous solution of ammonia there is only a small amount of $\text{NH}_4^+(\text{aq})$. Most of the ammonia is unreacted. This is indicated by the asymmetry of the double arrow. For this reason, NH_3 is said to be a *weak base*. In contrast, the reaction of NH_2^- with water shown above goes essentially to completion. NH_2^- is a *strong base*.

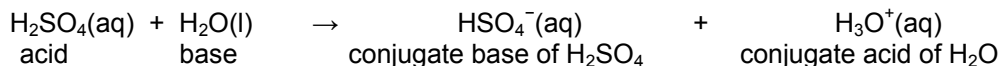
Acids are similarly labeled as strong or weak depending on whether the reaction with water goes to completion. For example, acetic acid is a *weak acid* (we use a double arrow):



Nitric acid is *strong acid* (we use a single arrow):

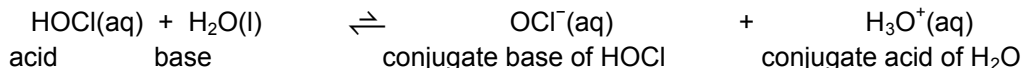


Note that the reverse of an acid base reaction is itself an acid base reaction. The acid and base of the reverse reaction are the products of the forward reaction – the result of the acid losing an H^+ and the result of the base having accepted an H^+ . These are called the conjugate base and conjugate acid, respectively. For example,



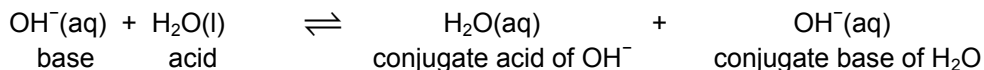
This reaction goes essentially to completion because H_2SO_4 is a stronger acid than H_3O^+ . The equilibrium is always shifted *away* from the stronger acid. Above, this corresponds to the forward reaction. This is why we call H_2SO_4 a *strong acid*.

In contrast,



Here, the acid HOCl is weaker than H_3O^+ (the reaction shifts away from the stronger acid). Hence, HOCl is called a *weak acid*.

Now consider some reactions of bases. When NaOH dissolves in water, we get $\text{OH}^-(\text{aq})$. Any alkali metal (Group 1) or alkaline earth (Group 2) metal hydroxide produces $\text{OH}^-(\text{aq})$ when dissolved in water. Let us consider what the reaction of the $\text{OH}^-(\text{aq})$ would be with water:



Here, the reactants and products are the same. This is a balanced equilibrium. The bases on both sides are the same and consequently equal in strength. We define OH^- to be a *strong base*. Any base stronger than OH^- , such as NH_2^- shown above, is also strong.

NH_3 , shown above, is a weak base. It is weaker than OH^- , as seen in the shift of the equilibrium towards reactants. The equilibrium is always shifted *away* from the stronger base. Note that this rule always agrees with the “*away* from the stronger acid” rule given above – we always see the stronger acid and the stronger base on the same side of the reaction. OCl^- is also weaker than OH^- , and is therefore a *weak base*.

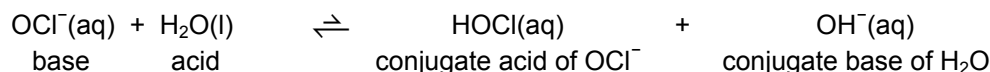


Table 3.1. Strong acids and a few weak acids

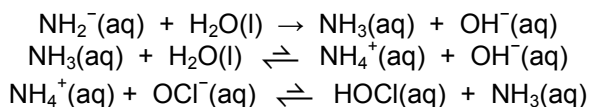
	Acid(s)	Conjugate Base(s)	
Strong Acids	HCl, HBr, HI	Cl^- , Br^- , I^-	The conjugate bases are very weak bases
	HNO_3	NO_3^-	
	H_2SO_4	HSO_4^-	
	HClO_3 , HClO_4	ClO_3^- , ClO_4^-	
Weak Acids	HF	F^-	The conjugate bases are weak bases
	HOCl	OCl^-	
	H_3PO_4	H_2PO_4^-	
	acetic acid:	CH_3COO^-	
	CH_3COOH		

Table 3.2. Strong bases and a few weak bases

	Base(s)	Conjugate Acid(s)	
Strong Bases	O^{2-} , oxide ion	OH^-	The conjugate acids are very weak acids
	(e.g. Li_2O , Na_2O , CaO , SrO)		
	OH^- , hydroxide ion	H_2O	
	(e.g. LiOH , NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$)		
	NH_2^- , amide ion	NH_3	
	(e.g. NaNH_2)		
	H^- , hydride ion	H_2	
	(e.g. LiH)		
Weak Bases	NH_3	NH_4^+	The conjugate acids are weak acids
	OCl^-	HOCl	
	methylamine:	CH_3NH_3^+	
	CH_3NH_2		

Note that weak acids are conjugate to weak bases, whereas **strong** acids are conjugate to **very weak** bases and **strong** bases are conjugate to **very weak** acids.

Example 3.2: Given that



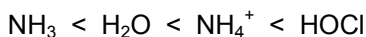
(a) Order the bases (the species acting as a base in either the forward or reverse of one of these reactions) according to increasing strength as a base (from weakest to strongest).

(b) Order the acids according to increasing strength.

- (a) In the first reaction, NH_2^- is the reactant base. This strongly product-favored reaction indicates that NH_2^- is a stronger base than OH^- . The shift to the left of the second equilibrium indicates that OH^- is a stronger base than NH_3 . The shift to the left of the third equilibrium indicates that NH_3 is a stronger base than OCl^- . Therefore, in order of increasing strength as a base, we have



- (b) The acids are just the conjugate acids to the bases listed. The order of acid strength is the reverse of the above order (with conjugate acids replacing the bases); i.e., according to strength as an acid,



3.3 Types of Acids and Bases

Binary Acids

The simplest class of acids is the binary acids consisting of H bonded to an electronegative atom. The most important of these are hydrosulfuric acid (H_2S), and the hydrohalic acids: hydrofluoric acid (HF), hydrochloric acid (HCl), hydrobromic acid (HBr) and hydroiodic acid (HI).

Oxoacids and Oxoanions

Many common acids are oxoacids. These are acids with a central atom bonded to one or more oxygen atoms, with one or more of those oxygen atoms in turn bonded to a hydrogen atom.⁵ The bases conjugate to the oxoacids are oxoanions. Some oxoacids can donate more than one H^+ - they are polyprotic. The common set of oxoacids and associated oxoanions are shown in Table 3.3.

⁵ There is one exception to this characterization of oxoacids: phosphorous acid (H_3PO_3), wherein a (non-acidic) H is bonded to the central atom - phosphorous in this case. However, the conjugate base rearranges such that both H atoms in H_2PO_3^- are bonded to an O. H_2PO_3^- is a diprotic acid that ultimately leads to PO_3^{3-} , the 3rd conjugate base of phosphorous acid.

Table 3.3. Oxoacids and oxoanions

Oxoacid	1 st Conjugate Base	2 nd Conjugate Base	3 rd Conjugate Base
H ₂ CO ₃ carbonic acid	HCO ₃ ⁻ hydrogen carbonate (bicarbonate)	CO ₃ ²⁻ carbonate	
HNO ₂ nitrous acid	NO ₂ ⁻ nitrite		
HNO ₃ nitric acid	NO ₃ ⁻ nitrate		
H ₃ PO ₃ phosphorous acid	H ₂ PO ₃ ⁻ dihydrogen phosphite	HPO ₃ ²⁻ hydrogen phosphite	PO ₃ ³⁻ phosphite
H ₃ PO ₄ phosphoric acid	H ₂ PO ₄ ⁻ dihydrogen phosphate	HPO ₄ ²⁻ hydrogen phosphate	PO ₄ ³⁻ phosphate
H ₂ SO ₃ sulfurous acid	HSO ₃ ⁻ hydrogen sulfite	SO ₃ ²⁻ sulfite	
H ₂ SO ₄ sulfuric acid	HSO ₄ ⁻ hydrogen sulfate	SO ₄ ²⁻ sulfate	
HClO hypochlorous acid	OCI ⁻ hypochlorite		
HClO ₂ chlorous acid	ClO ₂ ⁻ chlorite		
HClO ₃ chloric acid	ClO ₃ ⁻ chlorate		
HClO ₄ perchloric acid	ClO ₄ ⁻ perchlorate		

Note that some elements as central atoms (e.g. N, S, P and Cl) have more than one oxoacid. When there are two such species they are labeled ...ous acid and ...ic acid (e.g. nitrous and nitric acids). The oxoacid with more O atoms (for which the central atom has the highest oxidation number) is labeled ...ic acid, while that with fewer O atoms is labeled ...ous acid. The corresponding oxoanions are labeled ...ite and ...ate. In the case of chlorine, there are four oxoacids. The middle two (with respect to number of O atoms) acids are chlorous and chloric acid, respectively. That with one fewer O than chlorous acid is called hypochlorous acid. That with one more O than chloric acid is called perchloric acid. The conjugate base to hypochlorous acid is hypochlorite, while the conjugate base to perchloric acid is perchlorate. Other common oxoanions include the powerful oxidizing agents, dichromate, Cr₂O₇²⁻, and permanganate, MnO₄⁻.

Organic Acids and Bases

There are many organic acids. The simplest are the alkanolic (carboxylic) acids derived from the alkanes. The alkanes have the chemical formula, C_nH_{2n+2}. For example, for *n* = 1 and 2 we have methane, CH₄, and ethane, C₂H₆, respectively. The alkanolic acids are obtained by replacing 3 H atoms attached to one of the end carbon atoms with a doubly bonded O and an OH group (the O

bonds to the carbon atom. The result is a compound with formula, $C_nH_{2n-1}OOH$ (or $RCOOH$). The simplest of these compounds are tabulated in Table 3.4.

Simple amines are also derived from alkanes. We obtain an amine from an alkane by replacing an H with an NH_2 , to get a compound with chemical formula, $C_nH_{2n+1}NH_2$. The amines derived in this way are weak bases similar to ammonia. Some of them are tabulated in Table 3.4.

Table 3.4. Some simple organic acids and bases

Alkane	Alkanoic acid	Conjugate Base - Alkanoate	Amine
CH ₄ methane	HCOOH methanoic acid (also known as formic acid)	HCOO ⁻ methanoate (also known as formate)	CH ₃ NH ₂ methylamine
C ₂ H ₆ ethane	CH ₃ COOH ethanoic acid (also known as acetic acid)	CH ₃ COO ⁻ ethanoate (also known as acetate)	CH ₃ CH ₂ NH ₂ ethylamine
C ₃ H ₈ propane	CH ₃ CH ₂ COOH propanoic acid	CH ₃ CH ₂ COO ⁻ propanoate	CH ₃ CH ₂ NH ₂ Propylamine
C ₄ H ₁₀ butane	CH ₃ CH ₂ CH ₂ COOH butanoic acid	CH ₃ CH ₂ CH ₂ COO ⁻ butanoate	CH ₃ CH ₂ NH ₂ Butylamine
C ₅ H ₁₂ pentane	CH ₃ CH ₂ CH ₂ CH ₂ COOH pentanoic acid	CH ₃ CH ₂ CH ₂ CH ₂ COO ⁻ pentanoate	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ NH ₂ Pentylamine
C ₆ H ₁₄ hexane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COOH hexanoic acid	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COO ⁻ hexanoate	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ NH ₂ Hexylamine

Oxalic acid, $H_2C_2O_4$ is another related, commonly encountered, organic acid. It is a dicarboxylic acid. The associated 2nd conjugate base is oxalate, $C_2O_4^{2-}$.

Problems:

3.1 Which of the following reactions are acid-base reactions? For those that are acid-base reactions, identify the acid and the base.

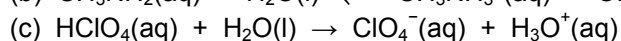
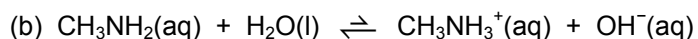
- (a) $2 Li(s) + Cl_2(g) \rightarrow 2 LiCl(s)$
- (b) $LiOH(aq) + HBr(g) \rightarrow LiBr(aq) + H_2O(l)$
- (c) $NH_3(aq) + HClO_3(aq) \rightarrow NH_4ClO_3(aq)$
- (d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- (e) $CH_3COOH(g) + NH_3(g) \rightarrow NH_4CH_3COO(s)$

3.2 Identify each of the following as a strong/weak acid/base, or neither acid nor base. What is the difference between a strong acid and a weak acid?

- (a) HF (b) CH₄ (c) KOH (d) CH₃NH₂ (e) HClO₄

3.3 Identify the conjugate acid base pairs present in the following reactions:

- (a) $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$



- 3.4 Some acids are cations, while some bases are anions. When we dissolve a salt in water, we get an acidic solution if the cation is an acid (strong or weak, but not very weak), and a basic solution if the anion is a base (strong or weak, but not very weak). If the salt is composed of an acid and a base, the pH of the resulting solution depends on the relative strength of the cation as acid and anion as base.

Which of the following salts will produce an acidic/basic solution when dissolved in water?

- (a) LiF (b) NH_4Cl (c) KBr (d) $\text{CH}_3\text{NH}_3\text{Cl}$ (e) NaOCl

- 3.5 Write out the chemical equilibria for the reactions of the acidic/basic ions (in question 3.4) with water. Indicate whether the equilibrium is shifted to the right or shifted to the left – i.e. use arrow size to depict the shift in equilibrium.