

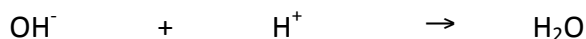
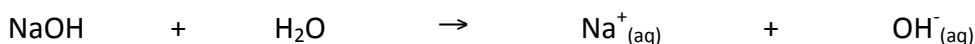
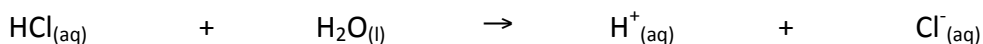
## 8.1 Theories of Acids and Bases

### Overview of The Three Theories

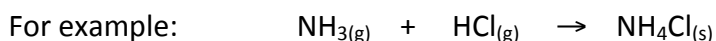
Theory	Acid	Base
Arrhenius	H <sup>+</sup> producer	OH <sup>-</sup> producer
Bronsted-Lowry	H <sup>+</sup> donor	H <sup>+</sup> acceptor
Lewis	Electron pair acceptor	Electron pair donor

### Arrhenius Theory

Svante Arrhenius in 1887 proposed the first theory describing acids and bases. Acids when dissolved in water break up into their respective ions of which one will be the **hydrogen, H<sup>+</sup> ion**. Hydrogen ions were referred to as *protons* because they are hydrogen atoms, which have lost an electron. Bases when dissolved in water break up into their constituent ions, one of which will be the **hydroxide ion, OH<sup>-</sup> ion**. The hydrogen and hydroxide ions could combine to form water.



Arrhenius' theory however was somewhat limited because it could not explain why acids and bases not in an aqueous solution did not produce hydrogen and hydroxide ions.



### Bronsted-Lowry Theory

In 1923 Bronsted and Lowry proposed an extension of Arrhenius theory that could describe how acids and bases not in solution reacted. Bronsted-Lowry acids and bases could be compounds, positive ions or negative ions. Bases did not have to contain hydroxide ions and water could act as an acid or a base.

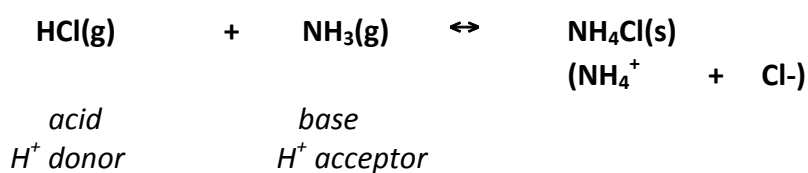
Bronsted-Lowry theory states that:

An acid produces protons (H<sup>+</sup> ions) and donates them to a base, which accepts it.  
**Therefore an acid is a proton donor and a base is a proton acceptor**

Acids and bases co-exist together as **conjugate pairs**.  
**Acid-base conjugate pairs are linked by a proton (H<sup>+</sup>)**

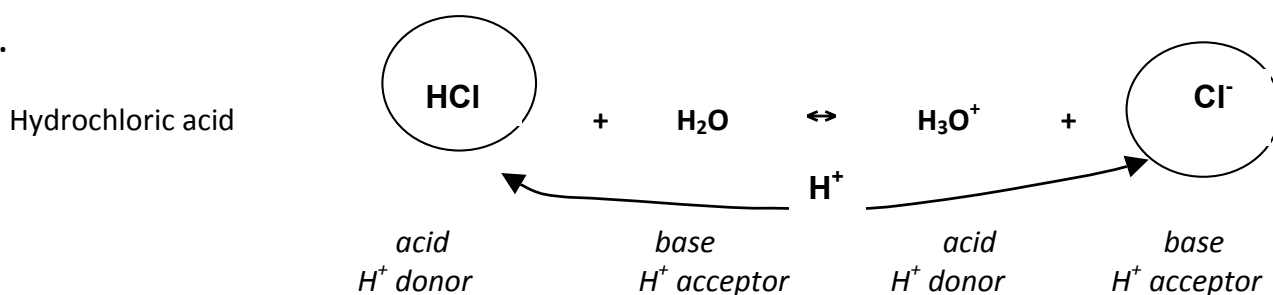
Examples

1. The reaction between gaseous ammonia and hydrogen chloride is considered a Bronsted-Lowry acid-base reaction because ammonia acts as a base or proton acceptor and hydrogen chloride an acid or proton donor.



- HCl is an B-L acid because it donates a proton to NH<sub>3</sub> to become NH<sub>4</sub>Cl
- NH<sub>3</sub> is a B-L base because it accepts a proton from HCl

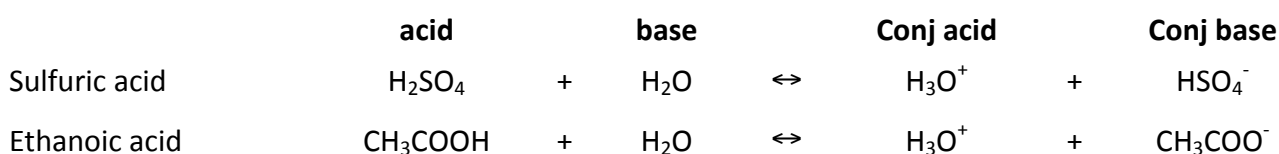
2.



- HCl is an B-L acid because it donates a proton. When the proton is donated it becomes Cl<sup>-</sup>.
- HCl and Cl<sup>-</sup> are called conjugate acid-base pairs.
- Cl<sup>-</sup> is a (conjugate) base because according to B-L theory it can accept a proton.
- H<sub>2</sub>O is a base because it accepts a proton becoming the acid, H<sub>3</sub>O<sup>+</sup>.
- H<sub>3</sub>O<sup>+</sup> is the conjugate acid of H<sub>2</sub>O because it is able to donate a proton.
- H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> are called conjugate acid-base pairs.

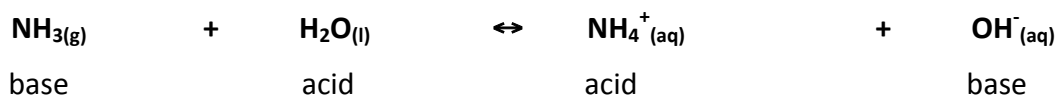
The H<sub>3</sub>O<sup>+</sup> ion is variously called the hydronium, hydroxonium, and oxonium ion. However, for convenience it is often just written as H<sup>+</sup><sub>(aq)</sub> in reactions.

Some other conjugate acid-base pairs:



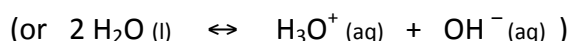
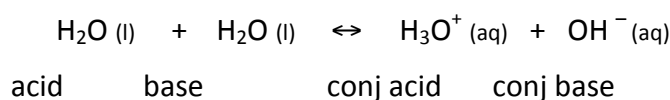
- An acid can only donate a proton if there is a base to accept it.
- B-L acids and bases are in equilibrium with one another, so a reaction will contain two acid-base conjugate pairs.
- The members of a conjugate acid-base pair always differ by a single proton. The acid has it and the base doesn't.
- To be able to accept a proton, a base must have a lone pair of electrons

3



- $\text{NH}_3$  is a base because it accepts a proton from  $\text{H}_2\text{O}$ . When the proton is accepted it becomes the conjugate acid  $\text{NH}_4^+$ .
- $\text{NH}_4^+$  is a conjugate acid because it is capable of donating a proton to form  $\text{NH}_3$ .
- $\text{NH}_3$  and  $\text{NH}_4^+$  are conjugate acid-base pairs.
- $\text{H}_2\text{O}$  is an acid because it donates a proton becoming the conjugate base,  $\text{OH}^-$ . As a (conjugate) base,  $\text{OH}^-$  can accept a proton to form  $\text{H}_2\text{O}$ .
- $\text{H}_2\text{O}$  and  $\text{OH}^-$  are called conjugate acid-base pairs.

Bronsted-Lowry theory can also be used to explain the dissociation or ionization of water. In B-L theory water dissociates when it reacts with itself. One water molecule acts as an acid because it accepts a proton,  $\text{H}^+$  from the other water molecule which acts as a proton acceptor or base to form  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ .



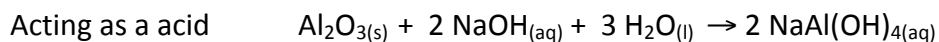
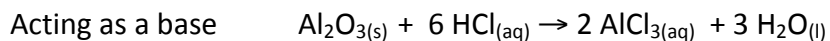
$$K_w = [\text{H}^+] \times [\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^\circ \text{ (298K)}$$

*Why do you think  $\text{H}_2\text{O}$  is not included in the water dissociation constant ( $K_w$ )?*

*What does the size of  $K_w$  tell you about the position of equilibrium?*

In Bronsted Lowry theory substances which can act as either a B-L acid or base are said to be **amphiprotic**. They can be proton acceptors or proton donors. Water is the most common example. Others include  $\text{HSO}_4^-$ ,  $\text{N}_2\text{H}_5^+$ ,  $\text{HCO}_3^-$ ,  $\text{HS}^-$ .

NOTE: The term 'amphoteric' is also used to describe a substance that can act as both acid and base. We used amphoteric to describe how aluminum oxide can act as both an acid and a base.



In Bronsted-Lowry theory:

**Monoprotic** – is the name given to an acid or base that donates or accepts one proton

**Diprotic** – is the name given to an acid or base that donates or accepts two protons

**Polyprotic** – is the name given to an acid or base that donates or accepts more than one proton

### Strength of B-L Acid-Base Conjugate Pairs

Generally:

Strong acids have weak conjugate bases

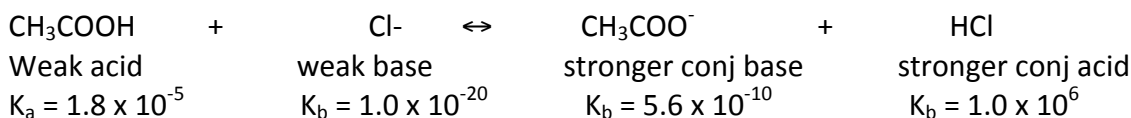
Weak acids have strong conjugate bases

1. Complete the table
2. Identify the species that are the strongest and weakest acids and bases

Formula	Name	$K_a$	Conjugate Base	$K_b$
HI	hydroiodic acid	$3.0 \times 10^9$	I <sup>-</sup>	$3 \times 10^{-24}$
HCl	hydrochloric acid	$1.0 \times 10^6$		$1.0 \times 10^{-20}$
H <sub>2</sub> SO <sub>4</sub>		$1.0 \times 10^3$	HSO <sub>4</sub> <sup>-</sup>	$1.0 \times 10^{-17}$
		55	H <sub>2</sub> O	$1.8 \times 10^{-16}$
HNO <sub>3</sub>		28		$3.6 \times 10^{-16}$
H <sub>3</sub> PO <sub>4</sub>		$7.1 \times 10^{-3}$	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$1.4 \times 10^{-12}$
		$1.8 \times 10^{-5}$	CH <sub>3</sub> COO <sup>-</sup>	$5.6 \times 10^{-10}$
H <sub>2</sub> S		$1.0 \times 10^{-7}$		$1.0 \times 10^{-7}$
	water	$1.8 \times 10^{-16}$	OH <sup>-</sup>	55
CH <sub>3</sub> OH		$1.0 \times 10^{-18}$		$1.0 \times 10^4$
H <sub>2</sub>		$1.0 \times 10^{-35}$	H <sup>-</sup>	$1.0 \times 10^{21}$
CH <sub>2</sub> =CH <sub>2</sub>		$1.0 \times 10^{-44}$	CH <sub>2</sub> =CH <sup>-</sup>	$1.0 \times 10^{30}$
CH <sub>4</sub>	methane	$1.0 \times 10^{-49}$		$1.0 \times 10^{35}$

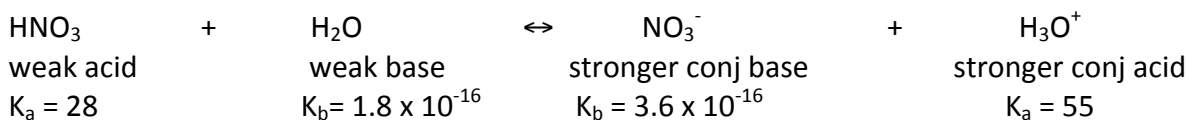
The strongest acids are on the top of the table and have the largest  $K_a$ . The strongest bases are the bottom of the table and have the largest,  $K_b$ . Each base is strong enough to accept a proton from the acid above it.

Consider the reaction:



The weak acid produces a stronger conjugate base than the reacting base. The weak base produces a stronger conjugate acid than the reacting acid.

In the example below the strong acid produces a conjugate base that is weaker than the reacting base. The weak base produces a stronger conjugate acid than the reacting acid.

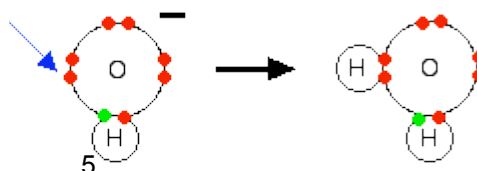
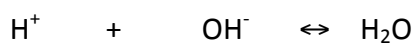


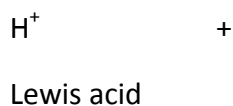
Using the table write a Bronsted Lowry reaction for an acid and a base of your choice. Identify the conjugate acid base pairs and identify as strong or weak.

## Lewis Theory

As useful as Bronsted-Lowry theory is it can't explain how or why these acid-base equilibrium reactions occur. This limitation was soon addressed by G.N Lewis. Lewis noticed that to be able to accept a proton all Bronsted-Lowry bases had a lone pair of electrons. He went one step further and thought of bases as electron pair donors and acids as electron pair acceptors. He used a mechanism (series of steps) involving curly arrows to show the transfer of electrons.

In Lewis theory bases are species with a non bonding pair of electrons which they donate to an acid. The bond formed between the acid and base is a coordinate covalent bond (dative bond).



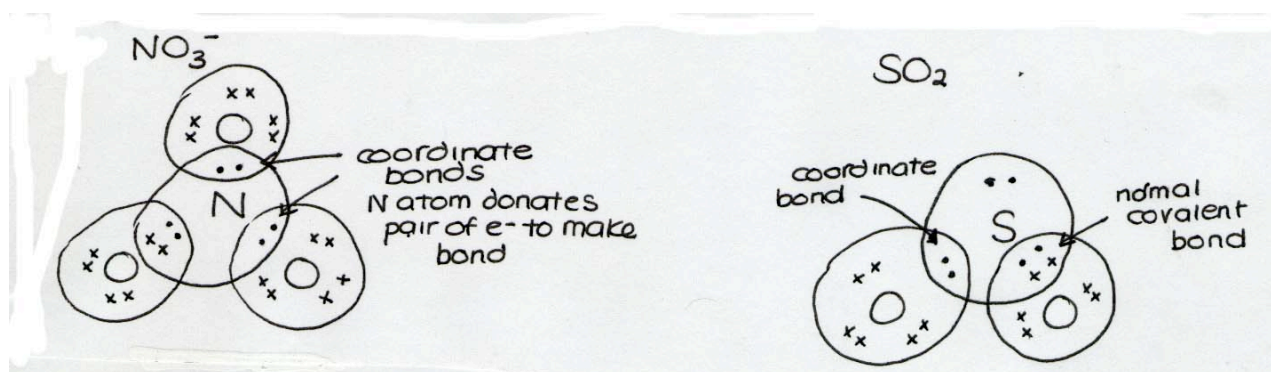


Lewis base

A non-bonding pair of electrons on the oxygen atom (shown by the arrow) of the hydroxide ion is donated to hydrogen ion.

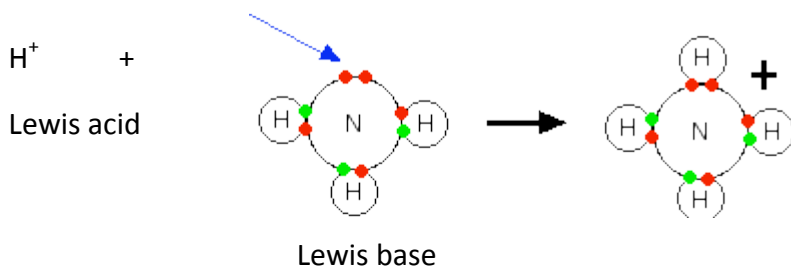
Circle the coordinate bond in water.

A **coordinate bond** (or dative bond) is a **covalent bond where one species provides the lone pair of electrons for the bond and the other species accepts it**. It is different from a normal covalent bond where both atoms contribute an equal number of electrons to the bond.



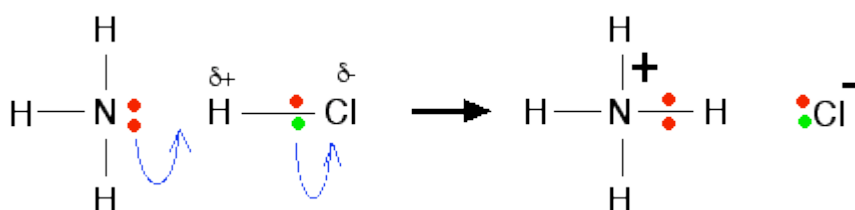
Lewis' theory complements Bronsted-Lowry theory by extending the range of acids and bases to include those that do not involve hydrogen or protons at all – like the boron trifluoride molecule,  $\text{BF}_3$ .

In the Lewis acid base reaction between a proton and ammonia the non-bonding pair of electrons on the nitrogen atom (shown by the arrow) of the ammonia is donated to the hydrogen ion



Circle the coordinate bond in the ammonium ion

When ammonia (Lewis base) reacts with hydrogen chloride (Lewis acid), in the mechanism the **curly arrows** show the movement of the pairs of electrons.



In summary, Lewis Theory states:

1. A **Lewis acid** accepts a pair of lone pair / nonbonding electrons to form a coordinate bond. It is an electron-pair acceptor. Examples include:
  - boron and aluminium halides like boron trifluoride,  $\text{BF}_3$ , aluminum chloride,  $\text{AlCl}_3$ ,
  - metal ions e.g.  $\text{Al}^{3+}$
  - transition metals e.g.  $\text{Cu}^{2+}$
  - $\text{H}^+$
  - Silicon compounds
  - $\text{SO}_3$
2. A **Lewis base** donates a lone pair/ non bonding electrons to form a coordinate covalent bond. It is an electron-pair donor. Examples include:
  - $\text{NH}_3$
  - $\text{OH}^-$
  - $\text{H}_3\text{O}^+$
  - $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$
  - $\text{O}^{2-}$
  - $\text{NH}_2^-$

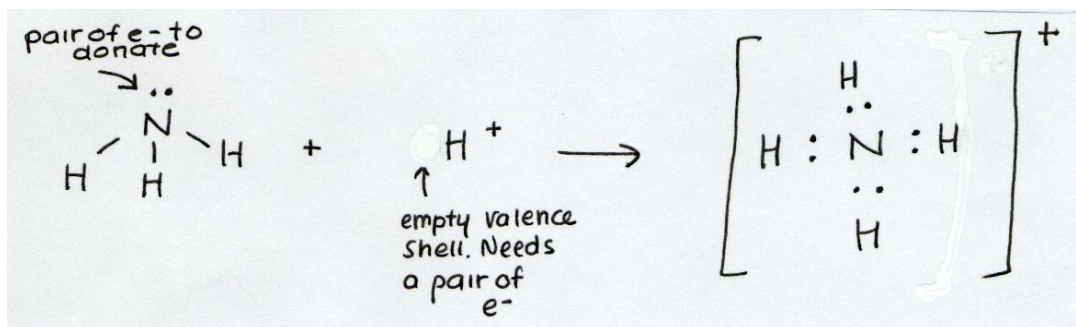
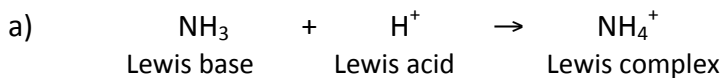
The Lewis theory has an advantage over the Bronsted-Lowry theory in that it covers many more molecules and reactions than Bronsted-Lowry.

### Some reactions of Lewis acids and bases

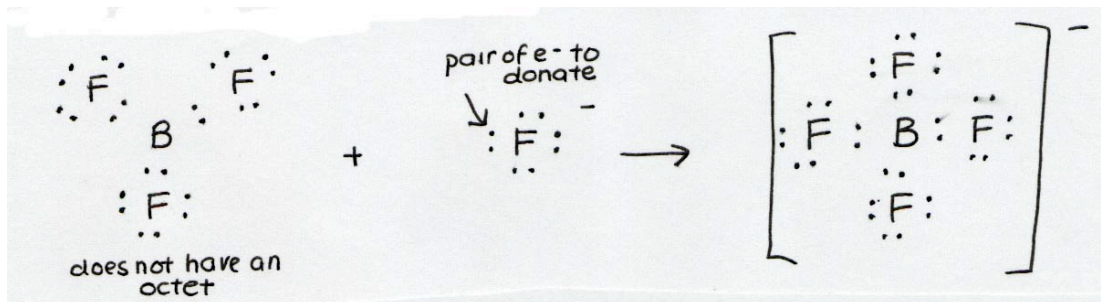
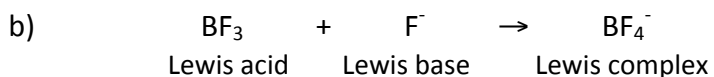
You will need to be able to write equations to illustrate Lewis Theory.

#### 1. Reactions between an acid and a base

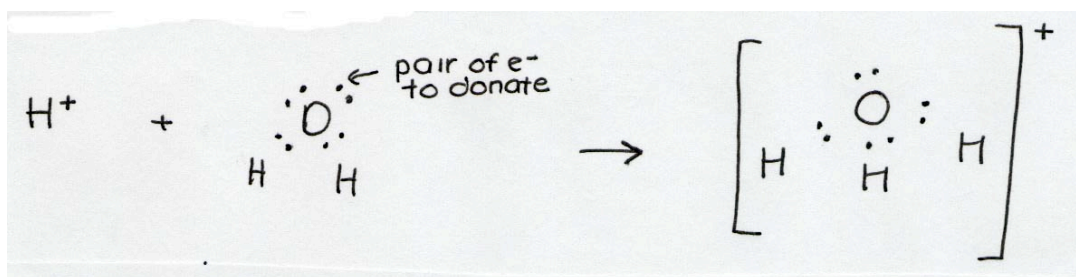
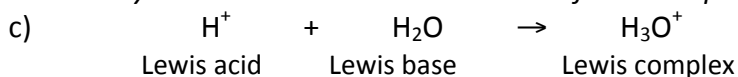
The Lewis acid base complexes formed are stable with an octet of electrons.



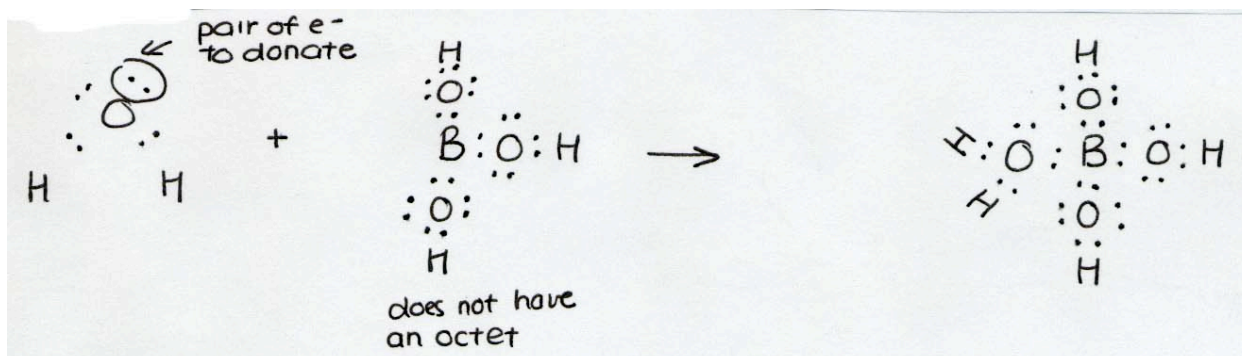
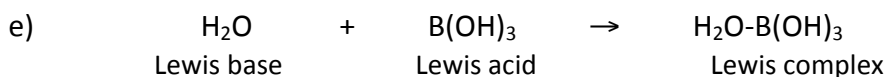
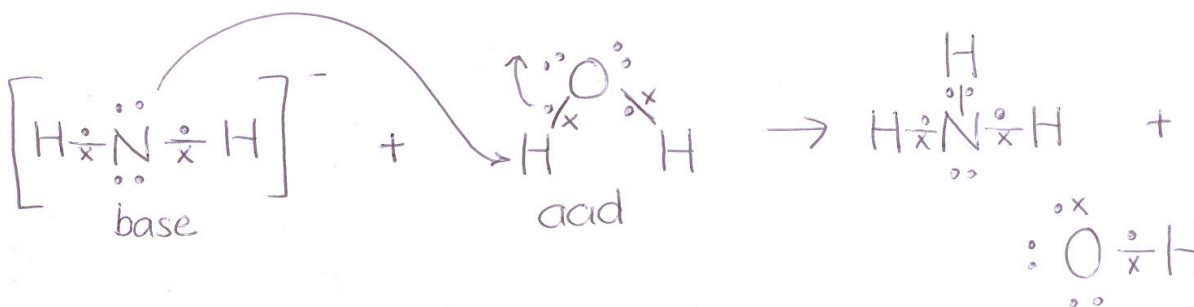
Draw curly arrows to show the movement of the lone pair of electrons.



Draw curly arrows to show the movement of the lone pair of electrons.

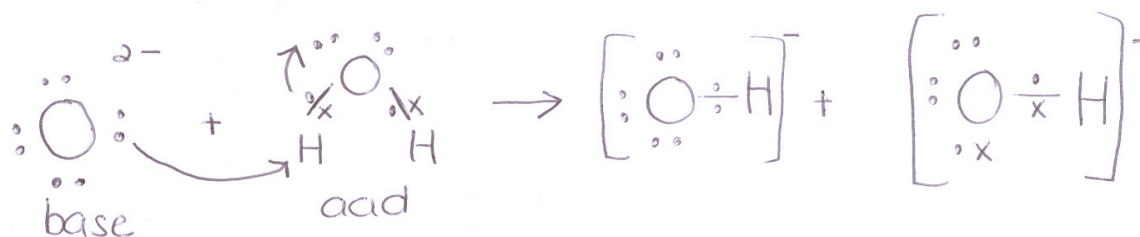
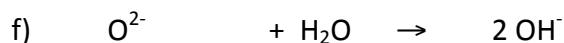


Draw curly arrows to show the movement of the lone pair of electrons.





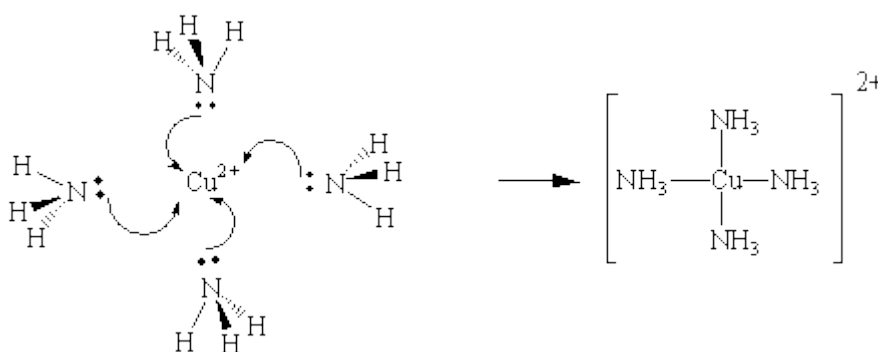
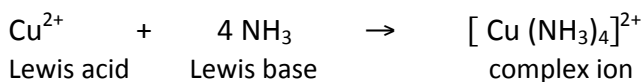
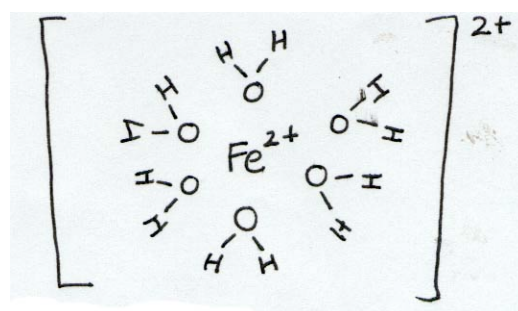
Draw curly arrows to show the movement of the lone pair of electrons.



## 2. (Higher Level) Formation of complex ions



The ligand is a Lewis base, which donates a lone pair of electrons. The ligand surrounds the metal ion in a fixed ratio. The metal ion and ligand form a dative (coordinate) bond. Typical ligands are  $H_2O$  and  $NH_3$ .



In the reaction mechanism curly arrows show the movement of the lone pair of electrons from the Lewis base to the Lewis acid.

Lewis acid-base theory can also be used to explain why acidic non-metal oxides such as  $SO_2$ ,  $SO_3$ ,  $NO$ ,  $NO_2$  and  $CO_2$  dissolve in water to form acids

## Comparing Bronsted-Lowry and Lewis Theories

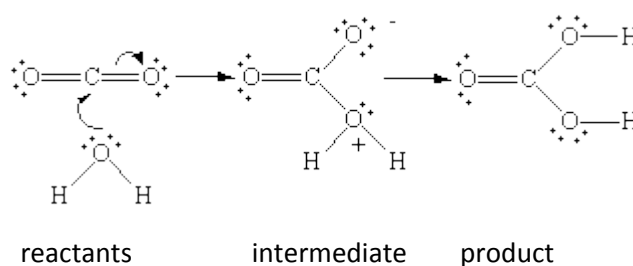
View the video on Lewis acids-base theory

<http://wps.pearsoned.com.au/ibcsl/89/22897/5861773.cw/index.html>

Account for why ammonia can be both a Lewis and Bronsted Lowry base.

Write an equation for the formation of carbonic acid from carbon dioxide and water. Identify the Lewis acid and Lewis base.

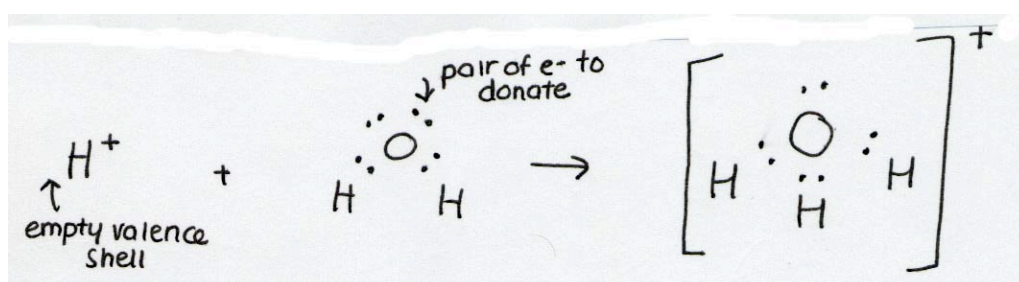
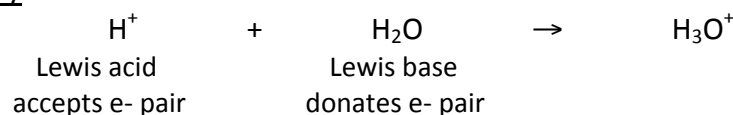
In the reaction between carbon dioxide and water when the carbon atom accepts a pair of electrons from the water molecule and intermediate complex is formed.



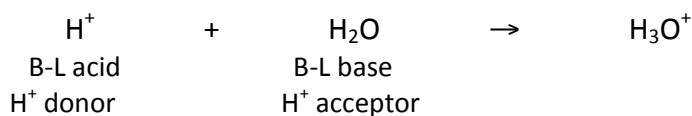
One of the oxygen atoms in the intermediate carries a positive charge and the other carries a negative charge. A hydrogen atom on the positively charged oxygen atom is transferred to the negatively charged oxygen atom to form the stable (electrically neutral) carbonic acid,  $\text{H}_2\text{CO}_3$  molecule.

Consider the following reaction:  $\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$

With Lewis Theory



### With Bronsted-Lowry Theory

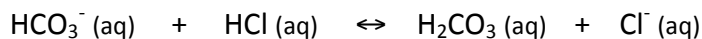


Although all Bronsted-Lowry acids are Lewis acids, not all Lewis acids are Bronsted-Lowry acids. The term Lewis acid is usually reserved for those species, which can only be described as electron pair acceptors that don't donate H<sup>+</sup> ions.

### Questions on Bronsted-Lowry Theory

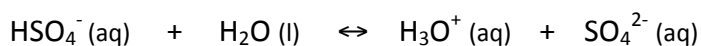
1. N02(S)

The relative strength of acids can be illustrated by the following equation.



- Identify the acid and its conjugate base and the base and its conjugate acid in the above equation.
- Name the theory that is illustrated in (i).

2. (M02/H&S) The ionization of sulfuric acid is represented by the equation below:



What is the conjugate base of the hydrogen sulfite ion, HSO<sub>4</sub><sup>-</sup> (aq)?

- H<sub>2</sub>O (l)
- H<sub>3</sub>O<sup>+</sup> (aq)
- H<sub>2</sub>SO<sub>4</sub> (aq)
- SO<sub>4</sub><sup>2-</sup> (aq)

3. M01(S)

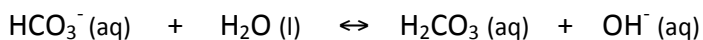
Which statement describes the Bronsted-Lowry behaviour of water molecules in aqueous solutions?

- They cannot act as either acids or bases

- B. They can act as acids but not as bases
- C. They can act as acids or bases when reacting with each other
- D. They can act as acids when reacting with HCl molecules

4. M01(S)

Sodium hydrogencarbonate dissolves in water forming an alkaline solution according to the following equilibrium:



- a) Why is the solution alkaline?
- b) Using the Bronsted-Lowry theory, state, with a brief explanation, whether the  $\text{HCO}_3^- (\text{aq})$  ion is behaving as an acid or a base.
- c) Identify the conjugate base of carbonic acid,  $\text{H}_2\text{CO}_3$

5. N98(S) The simplest amino acid has the structure  $\text{NH}_2\text{CH}_2\text{COOH}$ .

- a) Draw its structural formula (1)
- b) Circle and name the two functional groups. Identify them as acidic or basic. (4)
- c) Write the formula for its conjugate acid? (1)

6. Identify the acid/base conjugate pairs for:

- a)  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- b)  $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$
- c)  $\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + \text{H}_3\text{O}^+$
- d)  $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
- e)  $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$   
methylamine

7. Which one of the following statements about acids is untrue?

- A. acids are proton donors
- B. acids dissociate to form  $\text{H}^+$  ions if they dissolve in water
- C. Acids produce solutions with a pH greater than 7
- D. Acids will neutralize bases to form salts

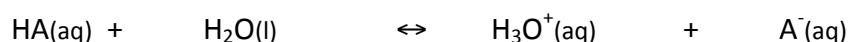
8. Substances can act as Bronsted-Lowry acids and/or bases if they give rise to a stable product. Identify the conjugate acid and base form of the following species and identify which of A-E is the most likely to be a Bronsted-Lowry acid or base.

- |    | Conjugate Acid  | conjugate Base |
|----|-----------------|----------------|
| A. | $\text{CH}_4$   |                |
| B. | $\text{NH}_4^+$ |                |

- C.  $\text{NH}_3$
- D.  $\text{H}_2\text{O}$

9. Draw Lewis dot diagrams for these Bronsted-Lowry bases. What do they have in common?
- a)  $\text{NH}_3$
  - b)  $\text{CH}_3\text{NH}_2$

10. (N02/S&H)  
Consider a weak acid HA dissolved in water:



Which statements are correct?

- I.  $\text{A}^-(\text{aq})$  is a much stronger base than  $\text{H}_2\text{O}(\text{l})$ .
  - II. HA dissociates only to a small extent in aqueous solution.
  - III. The concentration of  $\text{H}_3\text{O}^+(\text{aq})$  is much greater than the concentration of  $\text{HA}(\text{aq})$
- A. I, II and III
  - B. II and III only
  - C. I and II only
  - D. I and III only

11. (N05/H) The equilibrium reached when ethanoic acid is added to water can be represented by the following equation:



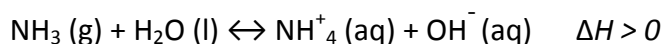
Identify the two Bronsted-Lowry acids and bases in this equation.

12. (M02/S) In aqueous solution, sodium hydroxide is a strong base and ammonia is a weak base. Use the Bronsted-Lowry theory to outline why both substances are classified as bases.

13. (M00/S)  $2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$   
The equilibrium constant for the reaction above is  $1.0 \times 10^{-14}$  at  $25^\circ\text{C}$  and  $2.1 \times 10^{-14}$  at  $20^\circ\text{C}$ . What can be concluded from this information?

- A.  $\text{H}_3\text{O}^+$  concentration decreases as the temperature decreases
- B.  $\text{H}_3\text{O}^+$  concentration is greater than  $\text{OH}^-$  concentration
- C. Water is a stronger electrolyte at  $25^\circ\text{C}$ .
- D. The ionization of water is endothermic

14. (N01) Which change increases the amount of  $\text{NH}_4^+$  ions in the reaction:



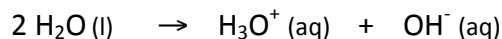
- A. decreasing the temperature
- B. decreasing the pressure
- C. removing water

D. adding an acid

15. N01(H) A Bronsted-Lowry base is defined as a substance which

- A. accepts  $H^+$  ions
- B. produces  $OH^-$  ions
- C. conducts electricity
- D. donates protons

16. M00(H) In the reaction:



- a) Use the Bronsted-Lowry definition to discuss the acidic and/or basic nature of water.
- b) What is the conjugate base of the hydroxide ion,  $OH^-(aq)$ ?

17. (M05/H) The equation for the reaction between nitric acid and sulfuric acid is shown below.



Which species are acting as acids in this reaction according to Bronsted-Lowry theory.

- A.  $H_2SO_4$  and  $HNO_3$
- B.  $H_2SO_4$  and  $H_2NO_3^+$
- C.  $HNO_3$  and  $H_2NO_3^+$
- D.  $H_2NO_3^+$  and  $HSO_4^-$

18. (M03/H) Which one of the following species can act as both a Bronsted-Lowry acid and base in aqueous solution.

- A.  $CH_3COOH$
- B.  $NO_3^-$
- C.  $H_2PO_4^-$
- D.  $OH^-$

19. Draw the Lewis structure for ammonia and circle the lone/non-bonding electron pair. Identify with a reason whether it is a Bronsted Lowry acid or base.

### Questions on Lewis Theory

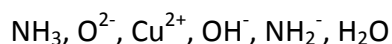
1. (M06/H)

Define the term Bronsted Lowry acid and Lewis acid. For each type of acid, identify one example other than water and write an equation to illustrate the definition. [5]

2. M06(H) Which species are a conjugate pair according to the Bronsted-Lowry theory?

- A.  $CH_3COOH$  and  $CH_3CHO^-$
- B.  $NH_3$  and  $BF_3$
- C.  $H_2NO_3^+$  and  $NO_3^-$
- D.  $H_2SO_4$  and  $HSO_4^-$

3. (M05/H) Choosing suitable examples from the following:



Explain using different equations in each case, the meaning of the terms below.

- (i) Bronsted-Lowry acid [2]  
 (ii) Lewis acid [2]  
 (iii) Conjugate acid-base pair (identify each member of both acid-base pairs) [3]

4. (M04/H) Which equation represents an acid-base reaction according to Lewis theory **but not** according to Bronsted-Lowry theory?

- A.  $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{l})$   
 B.  $\text{Ni}^{2+} + 6\text{H}_2\text{O} \rightarrow [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 C.  $\text{BaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$   
 D.  $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$

5. (M04/H) Which equation represents an acid-base reaction according to Lewis theory **but not** according to Bronsted-Lowry theory?

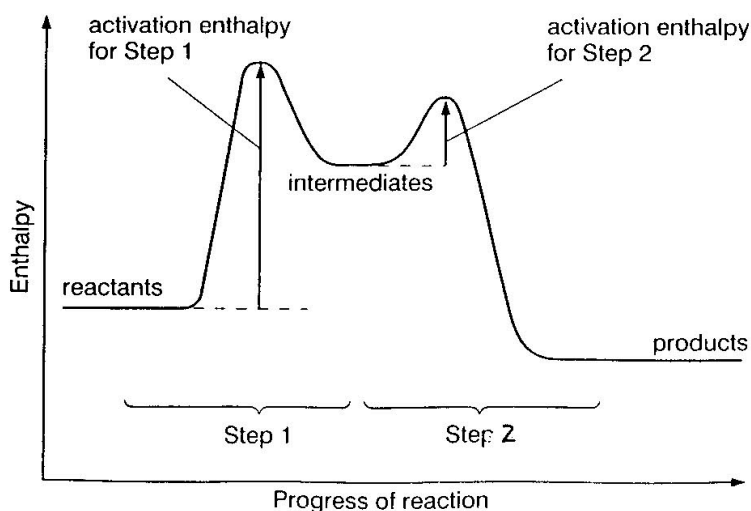
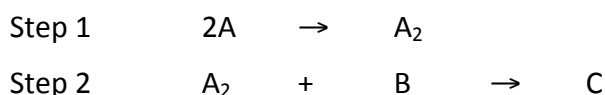
- A.  $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$   
 B.  $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$   
 C.  $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$   
 D.  $\text{CrCl}_3 + 6\text{NH}_3 \rightarrow [\text{Cr}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$

6. Today, all three theories of acids and bases are used by Chemists. Discuss the value of having three theories to explain acids and bases.

7. Draw Lewis dot diagrams for  $\text{BF}_3$  and  $\text{NH}_2^-$ . Identify with a reason whether they act as Lewis acids or bases.

### HL Questions only

8. a) Interpret the enthalpy diagram below.



b) State with a reason which step is the rate-determining step.

9. a) Define a ligand and complete the table of common ligands. (3)

Name	Formula	Charge on ligand
	H <sub>2</sub> O	
chloride ion		-1
ammonia	NH <sub>3</sub>	
	CN <sup>-</sup>	-1
hydroxide ion	OH <sup>-</sup>	

b) Draw and deduce the shape of the complex ion formed in the reaction (2)



c) What makes ligands good Lewis bases?

10. (N07/1) What is the oxidation state of cobalt in these complexes?

	[Co(NH <sub>3</sub> ) <sub>5</sub> Br]SO <sub>4</sub>	[Co(NH <sub>3</sub> ) <sub>5</sub> SO <sub>4</sub> ]Br
A	+3	+3
B	+2	+1
C	+3	+2
D	+2	+3

11. (N05/1) Which species can act as ligands in complex ion formation?

- I. Cl<sup>-</sup>
- II. NH<sub>3</sub>
- III. H<sub>2</sub>O

- A I and II only
- B I and III only
- C II and III only
- D I, II and III

12. (M05/1) Which is an essential feature of a ligand?

- A a negative charge
- B an odd number of electrons
- C the presence of two or more atoms



D the presence of a non-bonding pair of electrons