

# TABLE OF CONTENTS

<b>Preface, Acknowledgements, Cover photograph and Permissions</b>	<b>i</b>
--	----------

<b>Introduction</b>	<b>v</b>
---------------------	----------

## **UNIT I : REACTION KINETICS**

---

I.1. Introduction	1
I.2. Methods of Measuring Reaction Rates	2
I.3. Factors Affecting Reaction Rates	5
I.4. Experimental Measurement of Reaction Rates	11
I.5. Reaction Rates and Collision Theory	12
I.6. Enthalpy Changes in Chemical Reactions	13
I.7. Kinetic Energy Distributions	17
I.8. Activation Energies	20
I.9. Reaction Mechanisms	26
I.10. Energy Diagram of a Reaction Mechanism	29
I.11. The Effect of Catalysts on the Activation Energy	30
I.12. The Effect of a Catalyst on the Reaction Mechanism	32
I.13. Some Uses of Catalysts	34

## **UNIT II : EQUILIBRIUM**

---

II.1. The Concept of Dynamic Equilibrium	37
II.2. The Characteristics of Equilibrium	40
II.3. Predicting Whether a Reaction is Spontaneous or Not	43
II.4. Le Chatelier's Principle	50
II.5. Industrial Applications of Equilibrium Principles	56
II.6. The Equilibrium Expression and the Equilibrium Constant	57
II.7. Le Chatelier's Principle and the Equilibrium Constant	61
II.8. Equilibrium Calculations	63

## **UNIT III : SOLUBILITY EQUILIBRIUM**

---

III.1. A Review of Solubility	73
III.2. Calculating Solubility and Ion Concentrations	77
III.3. Predicting the Solubility of Salts	81
III.4. Writing Formula, Complete and Net Ionic Equations	84
III.5. Separating Mixtures of Ions by Precipitation Methods	88
III.6. The Solubility Product	91
III.7. Predicting Whether a Precipitate Will Form	96
III.8. Applying Solubility Principles to Chloride Titrations	99
III.9. Removing Pollution and Hardness from Water by Precipitation Methods	102
III.10. The Common Ion Effect and Others Ways to Alter the Solubility of a Salt	105

## UNIT IV : ACIDS, BASES AND SALTS

---

IV.1. The Arrhenius Theory of Acids and Bases	109
IV.2. Some Common Acids and Bases	112
IV.3. The True Nature of $H^+(aq)$ : (Background Theory)	115
IV.4. The Brønsted–Lowry Theory of Acids and Bases	116
IV.5. Conjugate Acids and Bases	119
IV.6. "Strong and Weak" Acids and Bases	121
IV.7. The Equilibrium Constant for the Ionization of Water	126
IV.8. $K_a$ and $K_b$	128
IV.9. The Relationship Between $K_a$ and $K_b$ for a Conjugate Pair	129
IV.10. The Relative Strengths of Acids and Bases	130
IV.11. pH and pOH	134
IV.12. Mixtures of Strong Acids and Bases	141
IV.13. Hydrolysis	144
IV.14. Calculations Involving $K_a$	148
IV.15. Calculations Involving $K_b$	152
IV.16. Acid–Base Titrations	154
IV.17. Indicators	159
IV.18. Practical Aspects of Titration	164
IV.19. Buffers	177
IV.20. Buffers in Biological Systems	182
IV.21. Applied Acid–Base Chemistry	184

## UNIT V : ELECTROCHEMISTRY

---

V.1. Introduction	189
V.2. Oxidation Numbers	193
V.3. Predicting the Spontaneity of a Redox Reaction	195
V.4. Balancing Half–Reactions	201
V.5. Balancing Redox Equations Using Half–Reactions	205
V.6. Balancing Redox Equations Using Oxidation Numbers	208
V.7. Redox Titrations	210
V.8. The Electrochemical Cell	215
V.9. Standard Reduction Potentials	218
V.10. Selecting Preferred Reactions	226
V.11. Applied Electrochemistry	228
V.12. Corrosion of Metals: Cause and Prevention	233
V.13. Electrolysis	237

### Answers

Answers to Unit I : Reaction Kinetics	249
Answers to Unit II : Equilibrium	257
Answers to Unit III : Solubility Equilibrium	267
Answers to Unit IV : Acids, Base and Salts	279
Answers to Unit V : Electrochemistry	301

<b>Glossary</b>	319
-----------------	-----

<b>Tables</b>	329
---------------	-----

## UNIT IV : ACIDS, BASES AND SALTS

In this unit you will study two theories about acids and bases. The first theory will cover most of what you already understand about acids and bases and the second one will be "built from scratch", based on your knowledge of equilibrium reactions. By the end of this unit you should appreciate the variety of effects that acid-base chemistry has on your life and be able to answer such questions as: How do our bodies protect us from the potentially lethal effects of eating pickles or tomatoes? (Aha! Now you're curious!) What causes "acid rain" and how might the damage it causes be prevented? Why do chickens who drink Perrier™ water give better eggs than chickens who drink ordinary water? How can you deal with a power-crazed Chemistry student who threatens to turn all the waters of the world into super-concentrated acid? Well, you'll never know the answers until you learn more, so let's get on with it.

### IV.1. THE ARRHENIUS THEORY OF ACIDS AND BASES

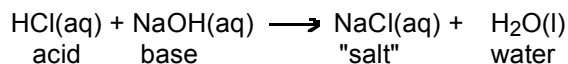
---

This theory of acids and bases is the first theory proposed to explain the actions of acids and bases, and is still valuable in many circumstances. The theory is named after Svante Arrhenius who did such outstanding work in developing the theory of electrolytes that he received the Nobel Prize in Chemistry in 1903. The following is actually a summary of the main ideas of his theory.

**Definitions:** An **ACID** is any substance which releases  $H^+(aq)$  in water.

A **BASE** is any substance which releases  $OH^-(aq)$  in water.

A **SALT** is the neutralization product which results when an acid and a base react.



In other words, a **SALT** is any **ionic** compound which is neither an acid nor a base.

OK, let's simplify this stuff a bit. The formal definitions are fine, but a little clumsy to use. The following is a simpler way to think of acids, bases and salts.

An **ACID** is any **ionic** species whose formula starts with an "H".

**EXAMPLES:** HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>

A **BASE** is any **ionic** species whose formula ends with an "OH".

**EXAMPLES:** NaOH, KOH, Ca(OH)<sub>2</sub>, Zn(OH)<sub>2</sub>

(There are exceptions to the idea that a formula which ends in "OH" must be a base, as will be seen later, but this is a reasonable way to recognize bases for now.)

The simplest way to recognize that a chemical is a salt is as follows. If the chemical is seen to be ionic because it contains species that you have come to recognize as being IONS, and if the formula DOES NOT START WITH "H" OR END WITH "OH", then you are dealing with a SALT.

**EXAMPLES:** **KBr**, **FePO<sub>4</sub>** and **Li<sub>2</sub>CO<sub>3</sub>**. These compounds contain species which are recognized as being ionic, such as  $K^+$ ,  $Br^-$ ,  $Fe^{3+}$ ,  $PO_4^{3-}$ ,  $Li^+$  and  $CO_3^{2-}$ . Also, none of the three compounds start with a "H" or end with an "OH", so ... these compounds are SALTS.

**EXERCISE:**

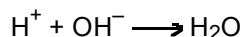
1. Which of the following are ACIDS, which are BASES, which are SALTS and which are NONE of these three categories?

- |                                      |                  |                             |                             |
|--------------------------------------|------------------|-----------------------------|-----------------------------|
| a) $\text{KNO}_3$                    | c) $\text{CH}_4$ | e) $\text{H}_2\text{CO}_3$  | g) $\text{Ba}(\text{OH})_2$ |
| b) $\text{HC}_2\text{H}_3\text{O}_2$ | d) $\text{LiOH}$ | f) $\text{Na}_2\text{CO}_3$ | h) $\text{SO}_2$            |

Next, we need to review how to write and balance an acid–base neutralization reaction. A general equation for the reaction between an acid and a base is:



All neutralization reactions are based on the fact that acids produce  $\text{H}^+$  and bases produce  $\text{OH}^-$ . The net ionic equation for every acid–base reaction just shows the production of water.



The following balancing procedure is used.

1. Check to see how many H's and OH's are in the formulae for the acid and base. For example, in the reaction:

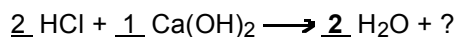


HCl can supply one H and  $\text{Ca}(\text{OH})_2$  can supply two OH's.

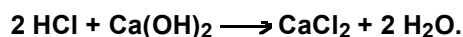
2. In front of the HCl and  $\text{Ca}(\text{OH})_2$  put the smallest coefficients which will give the same number (in this case, 2 and 1) of H's as OH's.



3. Since:  $\underline{1} \text{H}^+ + \underline{1} \text{OH}^- \longrightarrow \underline{1} \text{H}_2\text{O}$ , there are the same number of  $\text{H}_2\text{O}$ 's as H's (or OH's).



4. Finally, write down the formula for the salt produced by combining the remaining ions. The base contains  $\text{Ca}^{2+}$  and the acid contains  $\text{Cl}^-$ , and since the positive ion is ALWAYS written first in an ionic compound, start by writing: Ca Cl. Then, since 1 Ca atom and 2 Cl atoms exist on the reactant side, put these numbers after the appropriate atoms to create the formula for the salt:  $\text{Ca}_1\text{Cl}_2$ , or more correctly,  $\text{CaCl}_2$ . The final equation then becomes:

**EXERCISE:**

2. Balance the following neutralization equations.

- |   |  |
|---|--|
| a) $\text{H}_2\text{SO}_4$ reacts with NaOH                     | d) HCl reacts with $\text{Sn}(\text{OH})_4$                  |
| b) $\text{H}_2\text{SO}_4$ reacts with $\text{Fe}(\text{OH})_3$ | e) $\text{H}_2\text{S}$ reacts with $\text{Ca}(\text{OH})_2$ |
| c) $\text{H}_3\text{PO}_4$ reacts with KOH                      | f) $\text{H}_4\text{P}_2\text{O}_7$ reacts with NaOH         |

Now to finish examining the Arrhenius theory of acids and bases. Early chemists did not properly understand the nature of acids and bases. They decided if a substance was an acid or base by resorting to a method which works on the principle that "if it looks like a duck, quacks like a duck, flies like a duck and eventually produces more little ducks, then the thing is probably a duck". The following are termed **DESCRIPTIVE DEFINITIONS** of acids and bases.

**The presence of  $H^+$  accounts for the following properties of those substances which are traditionally called "acids".**

- a) acids react with bases
- b) acids are electrolytes
- c) acids act on some metals to produce  $H_2(g)$  (for example:  $Mg(s) + 2 HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$  )
- d) acids turn litmus paper RED
- e) acids taste SOUR (for example: vinegar, lemon juice)

**The presence of  $OH^-$  accounts for the following properties of those substances which are traditionally called "bases".**

- a) bases react with acids
- b) bases are electrolytes
- c) bases feel slippery (they react with your skin and fat to make soap)
- d) bases turn litmus paper BLUE
- e) bases taste BITTER (for example: baking soda)

Some comments on the above definitions are required.

1. Chemists DO NOT go around tasting everything they make in the lab (unless they have suicidal tendencies!), but early chemists **would** put a little of a particular chemical on their tongues to determine the taste, and then, without swallowing, rinse their mouths out before they poisoned themselves. What they did not appreciate is that some chemicals are **directly absorbed through the skin** ... and unfortunately early deaths among chemists were quite frequent. Moral: DON'T TASTE ANYTHING THAT ISN'T RECOGNIZED AS "FOOD".
2. Some metals, such as gold and platinum, are effectively unreactive with acids while other metals, such as sodium and potassium, are so reactive that they react with water. Magnesium is used to test for the presence of acids because it is just sufficiently reactive to produce  $H_2(g)$  when put into acids.
3. Remember that "BASES FEEL SLIPPERY"! If you ever get an unknown chemical on your hands and your hands feel slippery afterward, there is an excellent chance that you spilled a base on your hands. You must quickly wash **and** scrub your hands since the base starts to eat away the skin and form an outer layer which does not easily wash away. You have to scrub lightly to get to the base which is eating away **underneath** the "protective" outer layer.
4. A sneaky way to remember the litmus colours is shown below.

Litmus is:      RE      D      and      B      LUE In  
                   in ACID                                           BASE

**EXERCISES:**

3. Which of the following are properties of acids only, which are properties of bases only, which are properties of both, and which are not properties of either?
- |  |                          |
|--|--------------------------|
| a) form electrically conducting solutions in water | d) turn litmus paper red |
| b) react with metals to produce O <sub>2</sub> (g) | e) taste sour            |
| c) make skin feel slippery                         | f) react with salts      |
4. You have been given a solution and are told that it contains either an acid or base. What tests would you perform to help decide if the solution is acidic or basic?

**IV.2. SOME COMMON ACIDS AND BASES**

---

This Section outlines some common properties and uses of several important acids and bases.

**ACIDS**

- a) **Sulphuric Acid: H<sub>2</sub>SO<sub>4</sub>**    **Commercial names:** oil of vitriol, "battery acid"

**Properties:**

- good dehydrating agent (i.e. removes water from substances)
- strongly exothermic reaction when mixed with water
- concentrated form chars some types of organic material (e.g. sugars) as a result of dehydrating action
- reacts with some metals, but often slowly
- good electrolyte (conducts electricity)
- concentrated sulphuric acid is 98% H<sub>2</sub>SO<sub>4</sub> and 2% water (18 M H<sub>2</sub>SO<sub>4</sub>)

**Common uses:**

- production of sulphates
- manufacturing fertilizers, explosives, dyes, insecticides, detergents, plastics
- used to absorb water and keep chemicals/nonaqueous solutions free of water
- used in car batteries as an electrolyte

- b) **Hydrochloric Acid: HCl**    **Commercial name:** muriatic acid

**Properties:**

- good electrolyte
- concentrated solutions have a choking odour
- reacts with some metals, but often slowly
- concentrated hydrochloric acid is 37% HCl in water (12 M HCl)

**Common uses:**

- production of chlorides
- cleaning metal products (removes metal oxides) and bricks
- catalyst in some chemical reactions
- "stomach acid" is a dilute solution of HCl; stomach acid activates a protein-digesting biological catalyst called an "enzyme"
- removing "boiler scale", which consists of calcium and magnesium carbonate



c) **Nitric Acid:  $\text{HNO}_3$**     **Commercial name:** (none, other than "nitric acid")

**Properties:**

- colours protein yellow (this is a nonspecific test for the presence of protein). Hence, turns skin yellow on contact.
- very reactive, quickly attacks almost all metals
- concentrated nitric acid is 69%  $\text{HNO}_3$  in water (16 M  $\text{HNO}_3$ )

**Common uses:**

- production of nitrates
- manufacturing fertilizers, explosives, dyes

d) **Acetic Acid:  $\text{CH}_3\text{COOH}$**     **Commercial name:** 5% aqueous solution is called "vinegar"

**Properties:**

- non-electrolyte when concentrated (99 – 100%, 17 M); weak electrolyte when diluted
- only affects highly reactive metals

**Common uses:**

- making acetates
- food preservation ("pickles")
- manufacturing textiles and plastics

**BASES**

a) **Sodium Hydroxide: NaOH**    *Commercial names:* caustic soda, lye

**Properties:**

- very corrosive (caustic) to animal and plant tissues
- highly exothermic reaction when mixed with water
- rapidly "deliquesces"; that is, absorbs H<sub>2</sub>O from the air
- rapidly absorbs CO<sub>2</sub>(g) from the air to form carbonates:  $\text{NaOH(s)} + \text{CO}_2\text{(g)} \longrightarrow \text{NaHCO}_3\text{(s)}$

**Common uses:**

- making sodium salts
- making soap and other cleaning products such as oven cleaner, drain cleaner
- manufacturing glass, pulp and paper, plastics, aluminum
- neutralizing acids during industrial reactions

b) **Potassium Hydroxide: KOH**    *Commercial name:* caustic potash

**Properties:**

- much the same as NaOH, but melts at a lower temperature

**Common uses:**

- manufacturing liquid soap (potassium soaps have a lower melting temperature than sodium soaps)
- absorbing CO<sub>2</sub>(g)
- making potassium salts
- electrolyte in alkaline batteries

c) **Ammonia: NH<sub>3</sub>**    *Commercial name:* NH<sub>3</sub>(aq) is called "ammonium hydroxide"

**Properties:**

- colourless, alkaline, highly toxic, corrosive gas with pungent odour
- highly soluble in water
- exothermic reaction when dissolved in water

**Common uses:**

- manufacturing nitric acid
- manufacturing explosives, fertilizers, synthetic fibres
- used as a refrigeration gas

**EXERCISES:**

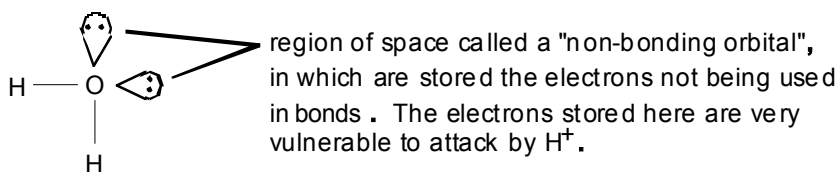
5. Why must containers of NaOH and KOH be tightly closed when not in use?
6. Which of the above acid and bases are useful in making: a) fertilizers?    b) plastics?
7. Which acid or base is used:
  - a) in car batteries?    c) as a refrigerant?    e) for cleaning fireplace bricks?
  - b) in making pickles?    d) in alkaline batteries?
8. Which of the above acids and bases could be used as drying agents?
9. Which of the above acids is the most reactive?



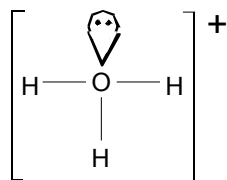
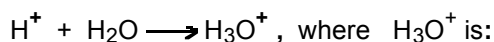
### IV.3. THE TRUE NATURE OF $H^+(aq)$ : (BACKGROUND THEORY)

The hydrogen atom consists of a proton surrounded by a single electron. If the electron is removed, so as to create  $H^+$ , a "naked" proton is left. Since this tiny nuclear particle has an enormous charge concentration (it has a +1 charge concentrated in a very small region of space — the diameter of a proton is  $5 \times 10^{-14}$  cm), this highly concentrated **positive** charge is **very strongly attracted** to any region where **negative** charges exist.

A water molecule has its electrons distributed as follows.



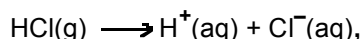
The attraction between  $H^+$  and the electrons in the non-bonding orbitals causes **all** the  $H^+$  ions present to attach themselves to available water molecules.



**Definition:**  $H^+$  is called the **proton**. (REMEMBER THIS !)  
 $H_3O^+$  is called the **hydronium ion**, or the **hydrated proton**.

Therefore, what has previously been called  $H^+(aq)$  is actually  $H_3O^+(aq)$ . Using  $H_3O^+(aq)$  instead of  $H^+(aq)$  will mean having to write the IONIZATION of an acid in another way.

**EXAMPLE:** When  $HCl(g)$  is added to water to produce  $HCl(aq)$ , the previous way of writing the dissociation:



is now rewritten as  $HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$ .

Notice that the second equation results from adding  $H_2O$  to both sides of the first equation, but on the right side the added  $H_2O$  combines with  $H^+$  to produce  $H_3O^+$ .

**EXERCISE:**

10. Write equations which show how the following acids dissociate in water to give  $H_3O^+(aq)$ .
- a)  $HNO_3(aq)$       b)  $HClO_4(aq)$

#### IV.4. THE BRØNSTED–LOWRY THEORY OF ACIDS AND BASES

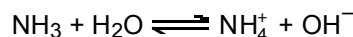
The Brønsted–Lowry theory is more *general* than the Arrhenius theory, and incorporates all of the Arrhenius theory into a larger scheme. The need to have another theory of acids and bases arose because of the existence of **EQUILIBRIUM** reactions, which were not considered when the original Arrhenius theory was proposed. Therefore, the Brønsted–Lowry theory is an expansion of the Arrhenius theory which allows for the existence of equilibrium reactions and an extension of the idea of acids and bases to a wider range of species and reactions.

##### Definitions:

An **ACID** is a substance which **DONATES A PROTON** to another substance.  
A **BASE** is a substance which **ACCEPTS A PROTON** from another substance.

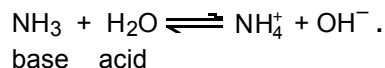
In other words: **an ACID is a PROTON DONOR** (gives away an  $H^+$ ), and  
**a BASE is a PROTON ACCEPTOR** (receives an  $H^+$ ).

Let's look at a typical Brønsted–Lowry acid–base reaction equation.



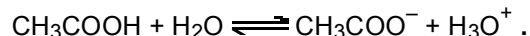
You should observe that the  $NH_3$  reacts to become  $NH_4^+$ . Hence, the  $NH_3$  has gained an extra "H" and a "+" charge, so that the  $NH_3$  **is acting as a BASE**: it has "accepted a proton" ( $H^+$ ).

WAIT, THERE'S MORE. If  $NH_3$  accepted a proton ( $H^+$ ) then  $H_2O$  must have donated a proton and acted as an ACID. If you examine the above equation again, you will see that the  $H_2O$  **has lost** (that is, donated) an  $H^+$ , and produced an  $OH^-$  in the process. Overall, then:



THE "TRICK" TO DECIDING WHETHER A SUBSTANCE IS ACTING AS AN ACID OR A BASE IS THIS: look at a particular chemical on the "REACTANT SIDE" of the equation and then look for a SOMEWHAT SIMILAR LOOKING chemical on the "PRODUCT SIDE". If the chemical on the PRODUCT side has ONE MORE H ATOM, then the REACTANT chemical must have GAINED (ACCEPTED) an  $H^+$ . If the chemical on the PRODUCT side has ONE LESS H ATOM, then the REACTANT chemical must have LOST (DONATED) an  $H^+$ .

Let's look at a second example.



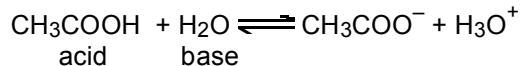
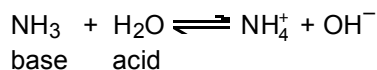
The  $CH_3COOH$  donates (loses) an  $H^+$  to become  $CH_3COO^-$  and therefore  $CH_3COOH$  must be acting as an ACID. (The fact that **acetic acid** acts as an acid should make sense!) The  $H_2O$  accepted a proton to become  $H_3O^+$  and hence  $H_2O$  must be acting as a BASE in this equation.

**Definitions:** A **MONOPROTIC ACID** is an acid which can supply only **one** proton.  
 A **DIPROTIC ACID** is an acid which can supply up to **two** protons.  
 A **TRIPROTIC ACID** is an acid which can supply up to **three** protons.  
 A **POLYPROTIC ACID** is a general term for an acid which can supply **more than one** proton.

**EXERCISES:**

11. In the following reactions, which reactant acts as an acid and which acts as a base?
- a)  $\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + \text{H}_3\text{O}^+$       d)  $\text{H}_3\text{PO}_4 + \text{CH}_3\text{COO}^- \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{CH}_3\text{COOH}$   
 b)  $\text{HCO}_3^- + \text{SO}_3^{2-} \rightleftharpoons \text{CO}_3^{2-} + \text{HSO}_3^-$       e)  $\text{CO}_3^{2-} + \text{HF} \rightleftharpoons \text{HCO}_3^- + \text{F}^-$   
 c)  $\text{HS}^- + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_2\text{S} + \text{HPO}_4^{2-}$
12. Consider the acids:  $\text{H}_3\text{PO}_4$ ,  $\text{HF}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_4\text{P}_2\text{O}_7$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCN}$ .
- a) Which of the acids are MONOPROTIC?      c) Which of the acids are TRIPROTIC?  
 b) Which of the acids are DIPROTIC?      d) Which of the acids are POLYPROTIC?

Let's go back a bit and look at the above two example equations.

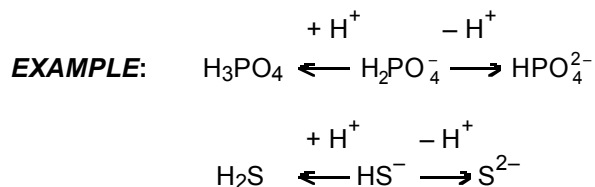


Oh, Oh ... this just got confusing: according to the Arrhenius theory,  $\text{H}_2\text{O}$  is neither an acid nor a base. But water acts as an **ACID** when it reacts with  $\text{NH}_3$  (in the first example) and as a **BASE** when it reacts with  $\text{CH}_3\text{COOH}$  (in the second example). Consider this question: when it comes to birthday presents, do you give or receive presents? It depends on whose birthday it is, doesn't it?

**CONCLUSION:** In some circumstances a substance acts as a Brønsted–Lowry acid, while in other circumstances the same substance acts as a Brønsted–Lowry base. Water acts as a Brønsted–Lowry base when it reacts with an acid and as an acid when it reacts with a base.

Water is an example of a substance which is said to be **AMPHIPROTIC**.

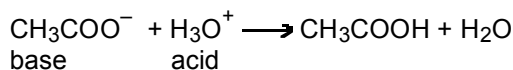
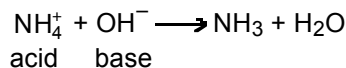
Some amphiprotic substances are:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HS}^-$  and  $\text{HCO}_3^-$ . Apart from  $\text{H}_2\text{O}$ , amphiprotic species are ions derived from POLYPROTIC ACIDS which have lost at least one proton. As shown in the example below, each ion can either lose another proton or regain one.



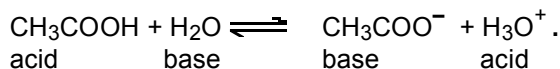
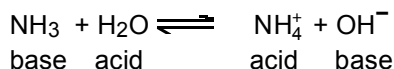
**CONCLUSION:** If a substance a) possesses a **NEGATIVE CHARGE**, and b) still has an easily removable **HYDROGEN**, then the substance will be **AMPHIPROTIC**.

(Apart from hydrogens attached to carbon, assume that all hydrogens on a negatively-charged ion are "easily removable".)

Examine another pair of Brønsted-Lowry acid-base reactions.

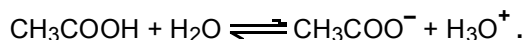


These reactions are the same as the two reactions at the start of this section, except that they are reversed. Since the reactions are reversible, the net result is:

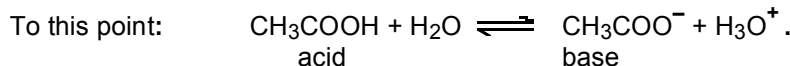


**In every Brønsted-Lowry reaction there is an acid and a base on both sides of the equation.**

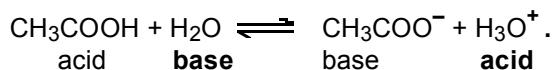
To save time deciding which species is which in a Brønsted-Lowry reaction, use the following procedure. In order to illustrate what is happening look at the example equation:



- First, determine the identity of one species on the reactant side, by seeing whether it gains or loses a proton. For example,  $\text{CH}_3\text{COOH}$  here is acting as an acid since it is losing a proton.
- Second, you can now determine the identity of the "similar species" on the product side. It is the opposite (for example, **BASE**) of the first species you identified (for example, **ACID**).



- Finally, use the fact that **each side must have both an ACID and a BASE** to complete the assignment. For example:



**EXERCISES:**

13. Identify each species in the following equations as being an acid or base.
- a)  $\text{HF} + \text{SO}_3^{2-} \rightleftharpoons \text{F}^- + \text{HSO}_3^-$       d)  $\text{H}_2\text{PO}_4^- + \text{S}^{2-} \rightleftharpoons \text{HS}^- + \text{HPO}_4^{2-}$
- b)  $\text{H}_2\text{O} + \text{HCO}_3^- \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$       e)  $\text{N}_2\text{H}_5^+ + \text{SO}_4^{2-} \rightleftharpoons \text{N}_2\text{H}_4 + \text{HSO}_4^-$
- c)  $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HNO}_2$
14. Which of the following would be expected to exhibit amphiprotic behaviour?  
 $\text{Se}^{2-}$ ,  $\text{HSe}^-$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HSO}_3^-$

**IV.5. CONJUGATE ACIDS AND BASES**

**Definitions:** A **CONJUGATE ACID–BASE PAIR** (or **CONJUGATE PAIR**) is a pair of chemical species which differ by only one proton.

A **CONJUGATE ACID** is the member of a conjugate pair which **HAS** the extra proton.

A **CONJUGATE BASE** is the member of a conjugate pair which **LACKS** the extra proton.

**EXAMPLE:** In the equilibrium reaction  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$  there are two conjugate pairs.

Conjugate pair	Conjugate acid	Conjugate base
$\text{NH}_4^+$ , $\text{NH}_3$	$\text{NH}_4^+$	$\text{NH}_3$
$\text{H}_2\text{O}$ , $\text{H}_3\text{O}^+$	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$

**EXERCISE:**

15. Write the appropriate species, taken from each conjugate pair, in the blanks provided.

	Conjugate pair	Conjugate acid	Conjugate base
a)	$\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$		
b)	$\text{HSO}_4^- / \text{SO}_4^{2-}$		
c)	$\text{PH}_3 / \text{PH}_4^+$		

**NOTE:** You can interpret the question "what is the conjugate base of X?" as "what base is the conjugate of X?" or "**what is the base counterpart of X?**".

All these statements imply that **X is an ACID.**

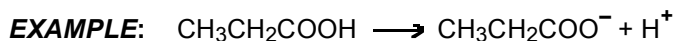
If you are asked to find the CONJUGATE ACID of  $\text{NH}_3$ , you should give the formula of the acid which has one MORE proton than  $\text{NH}_3$  (which is assumed to be a base).

Therefore, you add  $\text{H}^+$  to  $\text{NH}_3$  to get  $\text{NH}_4^+$ .

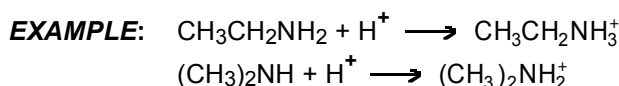
If you are asked to find the CONJUGATE BASE of  $\text{NH}_3$ , then you must give the formula of the base which has one LESS proton than  $\text{NH}_3$  (which is assumed to be an acid).

Therefore, you take away an  $\text{H}^+$  from  $\text{NH}_3$  to get  $\text{NH}_2^-$ .

**SPECIAL NOTE:** Simple **organic acids** end with a **COOH** group, and the H at the end of the group is acidic.



**Organic bases** contain an **NH<sub>2</sub>** group or an **NH** group. The **nitrogen** atom accepts  $\text{H}^+$ .

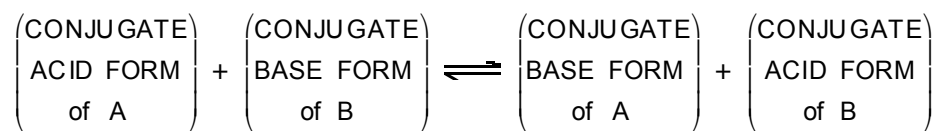


Using Lewis structures, the equilibrium reaction between water and  $\text{NH}_3$  is shown below.



Aha! Now you can see what is going on. There is an  $\text{H}^+$  which is just being tossed back and forth: from  $\text{H}_2\text{O}$  to  $\text{NH}_3$  and then from  $\text{NH}_4^+$  back to  $\text{OH}^-$ . You can imagine this "back-and-forth" motion by pretending that each of your hands is a different "base" molecule and that a can of "Chemi-Cola" is a proton. Take the can in your left hand. Since the left hand has the "proton", it is now an "acid" molecule. Toss the can over to your right hand. The left hand has lost its "proton" and is now a "base", whereas the right hand has gained a "proton" and is now an "acid". Each time the can is tossed back and forth, the "conjugate acid form" of a molecule turns into the "conjugate base form" of the molecule, and vice versa.

**CONCLUSION:** A Brønsted-Lowry acid-base reaction just involves an equilibrium proton transfer.



**EXAMPLE:** Write the acid-base equilibrium which occurs when  $\text{H}_2\text{S}$  and  $\text{CO}_3^{2-}$  are mixed in solution.

The  $\text{CO}_3^{2-}$  has no protons so it acts as a base. Since  $\text{CO}_3^{2-}$  is the base then  $\text{H}_2\text{S}$  will be the acid:



$\text{H}_2\text{S}$  donates a proton to become its conjugate base:  $\text{HS}^-$ .

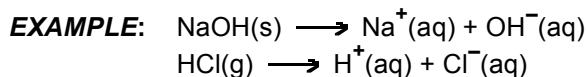
$\text{CO}_3^{2-}$  accepts a proton to become its conjugate acid:  $\text{HCO}_3^-$ .

**EXERCISES:**

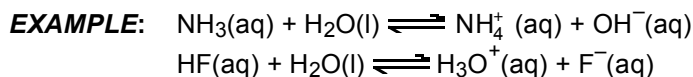
16. Write the formula for each of the following.
- a) the conjugate base of  $\text{HSO}_4^-$                       c) the conjugate base of  $\text{OH}^-$   
 b) the conjugate acid of  $\text{HSO}_4^-$                       d) the conjugate acid of  $\text{OH}^-$
17. Write the conjugate acid of each of the following.
- a)  $\text{F}^-$                       c)  $\text{Te}^{2-}$                       e)  $\text{HC}_2\text{O}_4^-$                       g)  $\text{H}^-$   
 b)  $\text{HTe}^-$                       d)  $\text{CH}_3\text{NH}_2$                       f)  $\text{H}_2\text{PO}_3^-$                       h)  $\text{N}_2\text{H}_4$
18. Write the conjugate base of each of the following.
- a)  $\text{H}_2\text{CO}_3$                       c)  $\text{HPO}_4^{2-}$                       e)  $\text{HN}_3$                       g)  $\text{HS}^-$   
 b)  $\text{C}_5\text{H}_5\text{NH}^+$                       d)  $\text{H}_2\text{O}_2$                       f)  $\text{HNO}_2$                       h)  $\text{C}_6\text{H}_5\text{COOH}$
19. Write the Brønsted–Lowry acid–base equilibria which occur when the following pairs of substances are mixed in solution.
- a)  $\text{HCN}$  and  $\text{F}^-$                       c)  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$                       e)  $\text{NO}_2^-$  and  $\text{HSO}_3^-$   
 b)  $\text{S}^{2-}$  and  $\text{HCOOH}$                       d)  $\text{HIO}_3$  and  $\text{C}_2\text{O}_4^{2-}$                       f)  $\text{HPO}_4^{2-}$  and  $\text{CH}_3\text{COO}^-$

**IV.6. "STRONG AND WEAK" ACIDS AND BASES**

**Definitions:** A **STRONG** acid or base is **100% ionized** in solution.

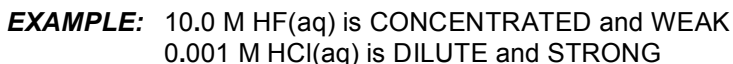


A **WEAK** acid or base is **LESS THAN 100% ionized** in solution.



- NOTE:**
- a) Equilibrium reactions involve **weak** acids and bases, **NOT strong** acids and bases.
- b) The definition of a weak acid implies that an acid which is 99% ionized is "weak", while an acid which is 100% ionized is "strong". This fine distinction won't cause any problems **in practice** because weak acids and bases are always less than 50% ionized.
- c) In everyday life the terms "**strong**" and "**concentrated**" are used interchangeably. For example: "I diluted the lemon juice because it was too strong". However, chemistry requires more precise terminology. Specifically ...

The terms WEAK and STRONG refer to the percentage of ionization.  
 The terms DILUTE and CONCENTRATED refer to the molarity of a solution.



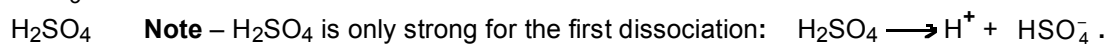
**EXERCISE:**

20. Suggest an experimental procedure to determine whether a 1 M aqueous solution of an unknown acid is strong or weak. (Hint: What you need is a method which can determine the difference between a solution which is 100% ionized and one which is less than 100% ionized. Titration won't work; whether or not the acid is weak or strong there is still 1 mol of acid in 1 L of the 1 M solution.)

At this point it is appropriate to introduce a table which will be very important in this unit. Look at the table of "Relative Strengths of Brønsted–Lowry Acids and Bases" at the back of this book as you read the following. (From now on we will refer to the table as "Relative Strengths of Acids" or occasionally as the "Table".

**THE STRONG ACIDS**

The strong acids are the **top six acids** on the **left** side of the table "Relative Strengths of Acids", namely:



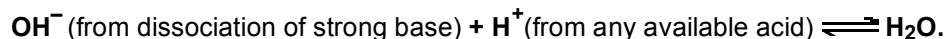
Notice that the top six reactions have ONE–WAY reaction arrows, pointing to the product side. This means the **REVERSE REACTIONS DO NOT OCCUR AT ALL** .

The 7th entry from the top,  $\text{H}_3\text{O}^+ \rightleftharpoons \text{H}^+ + \text{H}_2\text{O}$  , just shows that "H<sup>+</sup>(aq)" is equivalent to "H<sub>3</sub>O<sup>+</sup>(aq)". **This equilibrium is the net result of putting ANY strong acid in water:**

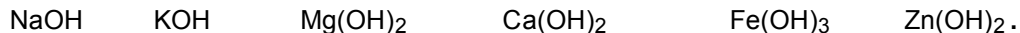
**THE STRONG BASES**

The **bottom two bases** listed on the **right** side of the table "Relative Strengths of Acids" are strong bases; that is, **O<sup>2-</sup>** and **NH<sub>2</sub><sup>-</sup>** are **strongly dissociated in water**.

The **3rd entry from the bottom**,  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  , is the result of adding **ANY strong base to water**:



The most common strong bases are metal hydroxides, which are 100% dissociated in water. For example:



Notice that the bottom two reactions on the Table have ONE–WAY reaction arrows, pointing BACKWARDS to the reactant side. This means the **FORWARD REACTIONS DO NOT OCCUR** .

**THE WEAK ACIDS**

The **weak acids** are the species on the **left** side of the Table from **HIO<sub>3</sub>** down to **H<sub>2</sub>O**. (H<sub>3</sub>O<sup>+</sup> is the result of adding a strong acid to water.)

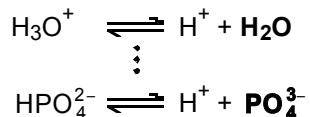


The weak acids on the left are always separated by equilibrium arrows from their conjugate bases on the right. **The last two species at the bottom left of the Table, OH<sup>-</sup> and NH<sub>3</sub>, NEVER act as acids in aqueous solutions.** (OH<sup>-</sup> and NH<sub>3</sub> can only be formed from the strong bases opposite them.)



**THE WEAK BASES**

The **weak bases** are the species on the **right** side of the Table from **H<sub>2</sub>O** down to **PO<sub>4</sub><sup>3-</sup>**. (OH<sup>-</sup> is the result of adding a strong base to water.)



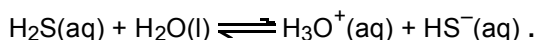
The weak bases on the right are separated by equilibrium arrows from their conjugates acids on the left.

**The six species (ClO<sub>4</sub><sup>-</sup> to HSO<sub>4</sub><sup>-</sup>) on the right of the top section of the Table NEVER act as bases in aqueous solutions;** they are the conjugates of strong acids.

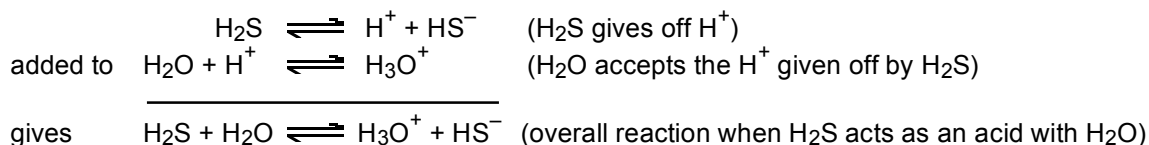
**A SPECIAL NOTE ON READING THE TABLE "RELATIVE STRENGTHS OF ACIDS"**

Looking at the Table you find, for example: **H<sub>2</sub>S**  $\rightleftharpoons$  **H<sup>+</sup>** + **HS<sup>-</sup>** .

This equation, being an equilibrium, may proceed forward or backward. When using the equation to refer to H<sub>2</sub>S acting as an acid in water, the equation should be written as:



The equation  $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$  is a simplified way to show what happens to H<sub>2</sub>S. The complete reaction is shown below.

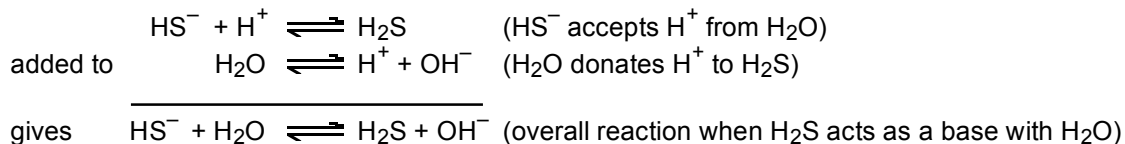


**When a substance acts as an acid with water, H<sub>3</sub>O<sup>+</sup> is always produced. The stronger the acid, the greater the [H<sub>3</sub>O<sup>+</sup>] produced.**

When using the equation to refer to HS<sup>-</sup> acting as a base, write the reaction in reverse, showing how HS<sup>-</sup> acts as a base with water:



The equation  $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$  is read in reverse to show what happens to HS<sup>-</sup>. The complete reaction is shown below.



**When a substance acts as a base with water, OH<sup>-</sup> is always produced. The stronger the base, the greater the [OH<sup>-</sup>] produced.**

### SOME OTHER RELATIONSHIPS FOUND IN THE TABLE

- The higher an acid is on the left side of the Table, the stronger the acid.

**Example:** HNO<sub>2</sub> is higher on the left side than HF, so HNO<sub>2</sub> is a stronger acid than HF.

- The lower a base is on the right side of the Table, the stronger the base.

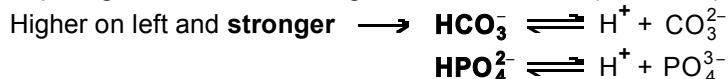
**Example:** HPO<sub>4</sub><sup>2-</sup> is lower on the right side than HCO<sub>3</sub><sup>-</sup>, so HPO<sub>4</sub><sup>2-</sup> is a stronger base than HCO<sub>3</sub><sup>-</sup>.

- The stronger an acid, the weaker its conjugate base, and vice versa.

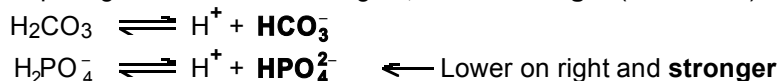
**Example:** HIO<sub>3</sub> is relatively strong for a "weak acid" but its conjugate base, IO<sub>3</sub><sup>-</sup>, is very weak.

**NOTE:** It is **NOT CORRECT** to say that, for example, since IO<sub>3</sub><sup>-</sup> is a very weak base then it is a relatively strong acid — IO<sub>3</sub><sup>-</sup> doesn't have any protons! It **IS CORRECT** to say that since IO<sub>3</sub><sup>-</sup> is a very weak base then **its conjugate acid, HIO<sub>3</sub>, is a relatively strong acid.**

**IMPORTANT:** HPO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> can be found on BOTH the left side AND the right side of the Table. When comparing relative **ACID** strengths, look at the **left (acid side)** of the Table.



When comparing relative **BASE** strengths, look at the **right (base side)** of the Table.



Water is amphiprotic: if mixed with a stronger acid than itself, water acts as a base; if mixed with a stronger base than itself, water acts as an acid.

### "THE LEVELLING EFFECT"

Examine the following results of preparing 1 M aqueous solutions of four different acids.

1 M HClO<sub>4</sub> produces: 1 M H<sub>3</sub>O<sup>+</sup> + 1 M ClO<sub>4</sub><sup>-</sup> (and **NO undissociated HClO<sub>4</sub>**)

1 M HCl produces: 1 M H<sub>3</sub>O<sup>+</sup> + 1 M Cl<sup>-</sup> (and **NO undissociated HCl**)

1 M HF produces: 0.97 M HF + 0.03 M H<sub>3</sub>O<sup>+</sup> + 0.03 M F<sup>-</sup>

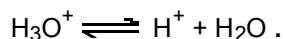
1 M CH<sub>3</sub>COOH produces: 0.996 M CH<sub>3</sub>COOH + 0.004 M H<sub>3</sub>O<sup>+</sup> + 0.004 M CH<sub>3</sub>COO<sup>-</sup>

The following points should be noticed.

- The weak acids (HF and CH<sub>3</sub>COOH) only dissociate to a small extent: the solutions still contain 0.97 mol of undissociated HF and 0.996 mol of undissociated CH<sub>3</sub>COOH.
- On the other hand, the strong acids (HClO<sub>4</sub> and HCl) produce solutions containing **NO** undissociated molecules of HClO<sub>4</sub> or HCl.
- HF and CH<sub>3</sub>COOH are both WEAK, but HF is "stronger" than CH<sub>3</sub>COOH, as can be seen from the fact that more H<sub>3</sub>O<sup>+</sup> is formed with HF than with CH<sub>3</sub>COOH.
- HClO<sub>4</sub> and HCl BOTH produce 1 M solutions of H<sub>3</sub>O<sup>+</sup>; in effect the HClO<sub>4</sub> and HCl solutions have been replaced by 1 M H<sub>3</sub>O<sup>+</sup> and another ion.

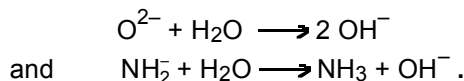
A look at the table of Relative Strengths of Acids shows that all the strong acids are 100% dissociated to form H<sub>3</sub>O<sup>+</sup>(aq). Water is said to have "levelled" all the strong acids to the same strength; they are all

solutions of  $\text{H}_3\text{O}^+$ (aq). Therefore,  $\text{H}_3\text{O}^+$  is the strongest acid which can exist in aqueous solution:



Because the table of Relative Strengths of Acids refers to **AQUEOUS SOLUTIONS**, do not make the mistake of thinking that the six acids at the top have different strengths. In fact, they have **IDENTICAL STRENGTHS** in aqueous solution and are equivalent to solutions of  $\text{H}_3\text{O}^+$ (aq).

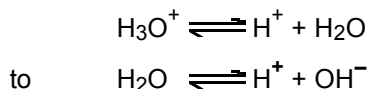
Similarly, the strongest base which can exist in aqueous solution is  $\text{OH}^-$ : all strong bases are 100% ionized to form  $\text{OH}^-$ . For example, the two strong bases shown at the bottom cannot exist in solution; they immediately undergo the following reactions on contact with water:



Do not make the mistake of thinking that  $\text{O}^{2-}$  and  $\text{NH}_2^-$  have different strengths in aqueous solutions.

**Definition: THE LEVELLING EFFECT** is the term describing the fact that all strong acids are 100% dissociated in aqueous solution and are equivalent to solutions of  $\text{H}_3\text{O}^+$ (aq), while all strong bases are 100% dissociated in aqueous solution and are equivalent to solutions of  $\text{OH}^-$ (aq).

Therefore, the central portion of the Table from:



shows the reactions which can actually occur in aqueous solution: the top six reactions are levelled to produce  $\text{H}_3\text{O}^+$  and the bottom two reactions are levelled to produce  $\text{OH}^-$ .

### EXERCISES:

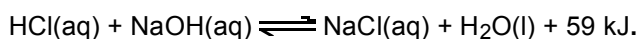
- Which member of each of the following pairs is the stronger acid?
  - $\text{HIO}_3$  or  $\text{CH}_3\text{COOH}$
  - $\text{H}_2\text{O}_2$  or  $\text{HSO}_3^-$
  - $\text{H}_2\text{PO}_4^-$  or  $\text{HCN}$
- Which member of each of the following pairs is the stronger base?
  - $\text{HCO}_3^-$  or  $\text{PO}_4^{3-}$
  - $\text{HPO}_4^{2-}$  or  $\text{HS}^-$
  - $\text{OH}^-$  or  $\text{NH}_3$
  - $\text{HCOO}^-$  or  $\text{HSO}_3^-$
- $\text{H}_2\text{Te}$  is a stronger acid than  $\text{H}_2\text{S}$ .
  - Write the formulae of the conjugate bases of the above two acids.
  - Which conjugate base is the stronger?
- Use the table "Relative Strengths of Acids" to write equations which show how the following reactions occur in water.
  - $\text{F}^-$  acts as a base
  - $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  acts as an acid
  - $\text{HCO}_3^-$  acts as an acid
  - $\text{HNO}_2$  acts as an acid
  - $\text{HCO}_3^-$  acts as a base
  - $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  acts as a base
- What is wrong with each of the following statements?
  - $\text{I}^-$  is on the right side of the table "Relative Strengths of Acids" (2nd entry from the top), and hence  $\text{I}^-$  acts as a base.
  - $\text{OH}^-$  is 2nd from the bottom on the acid side of the Table and 3rd from the bottom on the base side, and hence  $\text{OH}^-$  can act as either an acid or a base.
  - $\text{HClO}_4$  is stronger than  $\text{HBr}$  and therefore a 1 M solution of  $\text{HClO}_4$ (aq) is a stronger acid than a 1 M solution of  $\text{HBr}$ (aq).

26. Although HI is higher on the Table than HCl, explain clearly why 0.10 M HI(aq) and 0.10 M HCl(aq) both contain 0.10 M  $\text{H}_3\text{O}^+$ (aq).
27. How is it possible for a solution of a weak acid to have the same conductivity as a solution of a strong acid?

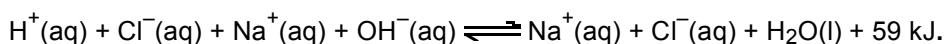
#### IV.7. THE EQUILIBRIUM CONSTANT FOR THE IONIZATION OF WATER

**Definitions:** A **NEUTRAL** solution is a solution having  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ .  
 An **ACIDIC** solution is a solution having  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ .  
 A **BASIC** solution is a solution having  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ .

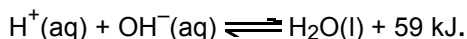
When a strong acid and a strong base react, a great deal of heat is released. For example:



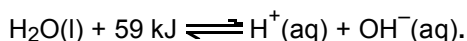
Re-writing this equation in complete ionic form gives



Eliminating the  $\text{Na}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  spectator ions gives the net ionic equation



This net ionic equation applies to the reaction between any strong acid and strong base. The reverse of this latter reaction is called the SELF-IONIZATION of water.



The equilibrium expression corresponding to the self-ionization reaction is

$$K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}).$$

(Recall that  $[\text{H}_2\text{O}(\text{l})]$  is a constant and is eliminated from the  $K_w$  expression.)

**NOTE:** The self-ionization of water can also be written as  $2 \text{H}_2\text{O}(\text{l}) + 59 \text{ kJ} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$  so that the equilibrium expression is

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}).$$

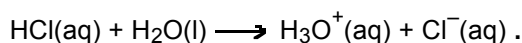
The equilibrium expression shows that  $[\text{H}_3\text{O}^+][\text{OH}^-]$  has a small, constant value: as  $[\text{H}_3\text{O}^+]$  increases,  $[\text{OH}^-]$  decreases, and vice versa.

**IMPORTANT:** Unless you are told otherwise, from now on you should always assume that the temperature is  $25^\circ\text{C}$ , and therefore the value of  $K_w$  is  $1.00 \times 10^{-14}$ .

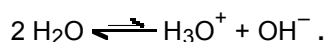
**EXERCISES:**

28. What is  $[\text{H}_3\text{O}^+]$  in pure, neutral water? What is  $[\text{OH}^-]$ ?
29. a) When water is heated, what happens to the  $[\text{H}_3\text{O}^+]$ ?  
 b) Is hot water acidic, basic or neutral?  
 c) What happens to the value of  $K_w$  when water is heated?

In 1 M HCl(aq), the HCl will be 100% ionized into 1 M  $\text{H}_3\text{O}^+$ (aq) and 1 M  $\text{Cl}^-$ (aq):



The concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in neutral water are very low:  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$  . The addition of excess  $\text{H}_3\text{O}^+$ (aq), from the HCl, neutralizes most of the  $\text{OH}^-$  present and shifts the equilibrium to form more water:



Nevertheless, even in acidic solutions a small amount of  $\text{OH}^-$  is always present. The added acid is not used up significantly by the small amount of  $\text{OH}^-$  initially present, so that the  $[\text{H}_3\text{O}^+]$  in the resulting solution remains at 1 M.

The equilibrium expression for water will play a major role in much of the remaining material in this section. One of the most common usages for the expression will be to solve for  $[\text{H}_3\text{O}^+]$  once  $[\text{OH}^-]$  is known, and vice versa.

**EXAMPLE:** What is  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in 0.0010 M HCl(aq)?

Since HCl is a strong acid, then  $[\text{H}_3\text{O}^+] = [\text{HCl}] = 1.0 \times 10^{-3} \text{ M}$

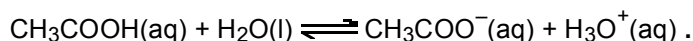
$$\text{and } [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11} \text{ M} .$$

**EXERCISE:**

30. Determine both  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in each of the following solutions.
- a) 10.0 M HCl    b) 4.0 M NaOH    c)  $2.5 \times 10^{-4} \text{ M HNO}_3$     d)  $6.00 \times 10^{-3} \text{ M Ca(OH)}_2$

### IV.8. $K_a$ AND $K_b$

The **ACID IONIZATION** reaction of a WEAK acid such as  $\text{CH}_3\text{COOH}$  with water is shown by



The equilibrium expression for the ionization is 
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.76 \times 10^{-5} .$$

(The equilibrium expression assumes that the solutions are sufficiently dilute that  $[\text{H}_2\text{O}]$  remains constant.)

The value of  $K_a$  is called the **ACID IONIZATION CONSTANT**.

The **BASE IONIZATION** reaction of a WEAK base such as  $\text{NH}_3$  with water is shown by



The equilibrium expression for the ionization is 
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.79 \times 10^{-5} .$$

The value of  $K_b$  is called the **BASE IONIZATION CONSTANT**.

The table of Relative Strengths of Acids shows that the greater the value of  $K_a$ , the stronger the acid. For a **STRONG ACID**, the value of  $K_a$  is not defined since the acid is 100% ionized and the concentration of the unionized acid in the denominator of the  $K_a$  expression is zero.

Similarly, the greater the  $K_b$  value for a base, the stronger the base. The table of Relative Strengths of Acids does not list  $K_b$  values but the next section shows the procedure for calculating  $K_b$  values using  $K_a$  values in the Table.

#### EXERCISES:

31. Write the  $K_a$  expression for the reaction in which each of the following acts as an acid with water.
  - a)  $\text{HCN}$
  - b)  $\text{HPO}_4^{2-}$
  - c)  $\text{HNO}_2$
32. Write the  $K_b$  expression for the reaction in which each of the following acts as a base with water.
  - a)  $\text{HS}^-$
  - b)  $\text{CH}_3\text{NH}_2$
  - c)  $\text{F}^-$
33. You have a 1 M solution of an acid with  $K_a = 1 \times 10^{-5}$  and a 1 M solution of an acid with  $K_a = 1 \times 10^{-10}$ . Which solution contains the greater concentration of  $\text{H}_3\text{O}^+$ ?
34. You have a 1 M solution of a base with  $K_b = 5 \times 10^{-12}$  and a 1 M solution of a second base with  $K_b = 7 \times 10^{-6}$ . Which solution contains the greater concentration of  $\text{OH}^-$ ?

### IV.9. THE RELATIONSHIP BETWEEN $K_a$ AND $K_b$ FOR A CONJUGATE PAIR

Experimentally, it is found that the **ACID IONIZATION** equation  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

has the acid ionization constant  $K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = 5.59 \times 10^{-10}$ ,

while the **BASE IONIZATION** equation  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

has the base ionization constant  $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.79 \times 10^{-5}$ .

Since both equations involve  $\text{NH}_3$  and  $\text{NH}_4^+$ , you might suspect that there is some relationship between  $K_a$  and  $K_b$  for these species. In fact

$$K_a \times K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-].$$

CONCLUSION: for a **CONJUGATE PAIR**

$$K_a(\text{conjugate acid}) \times K_b(\text{conjugate base}) = K_w.$$

This equation allows you to find  $K_b$  values for weak bases on the table of Relative Strengths of Acids.

**EXAMPLE:** To FIND the  $K_a$  value for  $\text{H}_2\text{PO}_4^-$  look down the **LEFT** side (that is, the **ACID** side) of the Table until you find  $\text{H}_2\text{PO}_4^-$ .



The  $K_a$  for  $\text{H}_2\text{PO}_4^-$  is immediately seen to be  $6.2 \times 10^{-8}$ .

To CALCULATE the  $K_b$  value for  $\text{H}_2\text{PO}_4^-$  look down the **RIGHT** side (that is, the **BASE** side) of the Table until you find  $\text{H}_2\text{PO}_4^-$ .



Since this equation should be read as  $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_4 + \text{OH}^-$  when  $\text{H}_2\text{PO}_4^-$  acts as a base, the base ionization constant can be calculated from:

$$K_b(\text{H}_2\text{PO}_4^-) = \frac{K_w}{K_a(\text{H}_3\text{PO}_4)} = \frac{1.00 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12}.$$

**EXERCISES:**

35. Use your table of Relative Strengths of Acids to calculate  $K_b$  for the following bases.
- |  |                        |                     |
|--|------------------------|---------------------|
| a) $\text{SO}_4^{2-}$                                | c) $\text{HCO}_3^-$    | e) $\text{HSO}_3^-$ |
| b) $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ | d) $\text{HPO}_4^{2-}$ | f) $\text{HS}^-$    |
36. Given that  $K_b = 1.7 \times 10^{-6}$  for  $\text{N}_2\text{H}_4$ , what is  $K_a$  for  $\text{N}_2\text{H}_5^+$  ?
37. If a substance has a  $K_b$  value of  $2 \times 10^{-10}$ , is the substance a weak acid, a strong acid, a weak base or a strong base? Explain your answer.

**IV.10. THE RELATIVE STRENGTHS OF ACIDS AND BASES**

If solutions containing  $\text{H}_2\text{CO}_3$  and  $\text{SO}_3^{2-}$  are mixed, the  $\text{SO}_3^{2-}$  can only act as a base since it has no protons.



so that there are again 2 conjugate pairs in solution.

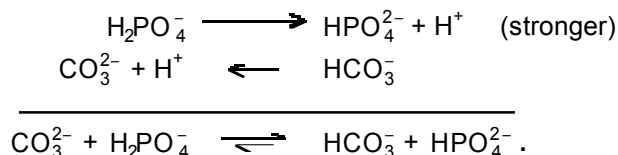
**NOTE:** All the Brønsted–Lowry reactions studied in Chem 12 will only involve the transfer of a single proton. There will **NOT** be two–proton transfers such as



Now consider what happens when  $\text{CO}_3^{2-}$  and  $\text{H}_2\text{PO}_4^-$  are mixed.



A "proton competition" is now set up in solution. There are two acids in equilibrium,  $\text{H}_2\text{PO}_4^-$  and  $\text{HCO}_3^-$ , each of which can donate a proton. Conversely, there are two bases in solution, each of which can accept a proton. Reasonably, the stronger of the two acids involved will be more successful in donating a proton than the weaker. From the table of Relative Strengths of Acids it can be seen that  $\text{H}_2\text{PO}_4^-$  ( $K_a = 6.2 \times 10^{-8}$ ) is stronger than  $\text{HCO}_3^-$  ( $K_a = 5.6 \times 10^{-11}$ ), so that:



As a result,  $\text{H}_2\text{PO}_4^-$  has a greater tendency to donate a proton than does  $\text{HCO}_3^-$ . Therefore, there will be more products than reactants ("products are favoured").

**To Summarize:** In a Brønsted–Lowry acid–base equilibrium, the side of the equilibrium which has the **WEAKER ACID** will be "favoured".



There is also a different way to show that products are favoured in the above reaction. [You are not required to know both methods. Both methods can be used to describe whether reactants or products are favoured in a reaction, so pick the method you like better.]

Since the above reaction is an equilibrium, the equilibrium expression for it is:

$$K_{\text{eq}} = \frac{[\text{HCO}_3^-][\text{HPO}_4^{2-}]}{[\text{CO}_3^{2-}][\text{H}_2\text{PO}_4^-]}$$

This expression can be rewritten as follows

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \times \frac{[\text{HCO}_3^-]}{[\text{H}^+][\text{CO}_3^{2-}]} = K_{\text{a}}(\text{H}_2\text{PO}_4^-) \times \frac{1}{K_{\text{a}}(\text{HCO}_3^-)}$$

or simply 
$$K_{\text{eq}} = \frac{K_{\text{a}}(\text{H}_2\text{PO}_4^-)}{K_{\text{a}}(\text{HCO}_3^-)} .$$

Evaluating this expression: 
$$K_{\text{eq}} = \frac{6.2 \times 10^{-8}}{5.6 \times 10^{-11}} = 1.1 \times 10^3 = \frac{[\text{products}]}{[\text{reactants}]} .$$

This value agrees with the prediction: there should be more products than reactants if  $K_{\text{eq}} > 1$ .

**NOTE:** A general expression for calculating the equilibrium value can be derived, based on the  $K_{\text{a}}$  values of the acids involved in the reaction.

Let  $K_{\text{a}}(\text{reactant acid})$  = the  $K_{\text{a}}$  value of the acid on the reactant side, **HReact**

$K_{\text{a}}(\text{product acid})$  = the  $K_{\text{a}}$  value of the acid on the product side, **HProd**

Then for the reaction: **HReact + Prod<sup>-</sup> ⇌ React<sup>-</sup> + HProd** the equilibrium expression is:

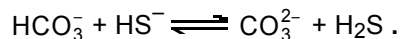
$$K_{\text{eq}} = \frac{K_{\text{a}}(\text{reactant acid})}{K_{\text{a}}(\text{product acid})} .$$

**Important:** Be sure that you understand the significance of the above expression.  **$K_{\text{eq}}$  is the ratio of [products] to [reactants]**, and its value **ALSO** can be calculated as the ratio of the  $K_{\text{a}}$  value for the reactant acid to the  $K_{\text{a}}$  value for the product acid.

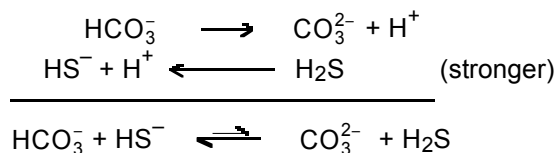
$$\frac{[\text{products}]}{[\text{reactants}]} = K_{\text{eq}} = \frac{K_{\text{a}}(\text{reactant acid})}{K_{\text{a}}(\text{product acid})} .$$

**EXAMPLE:** When  $\text{HS}^-$  and  $\text{HCO}_3^-$  are mixed, does the resulting equilibrium favour reactants or products?

Since  $\text{HCO}_3^-$  is a stronger acid than  $\text{HS}^-$ , then  $\text{HS}^-$  acts as a base and the equilibrium is written as



The two acids are  $\text{HCO}_3^-$  and  $\text{H}_2\text{S}$ ;  $\text{H}_2\text{S}$  is a stronger acid than  $\text{HCO}_3^-$ .

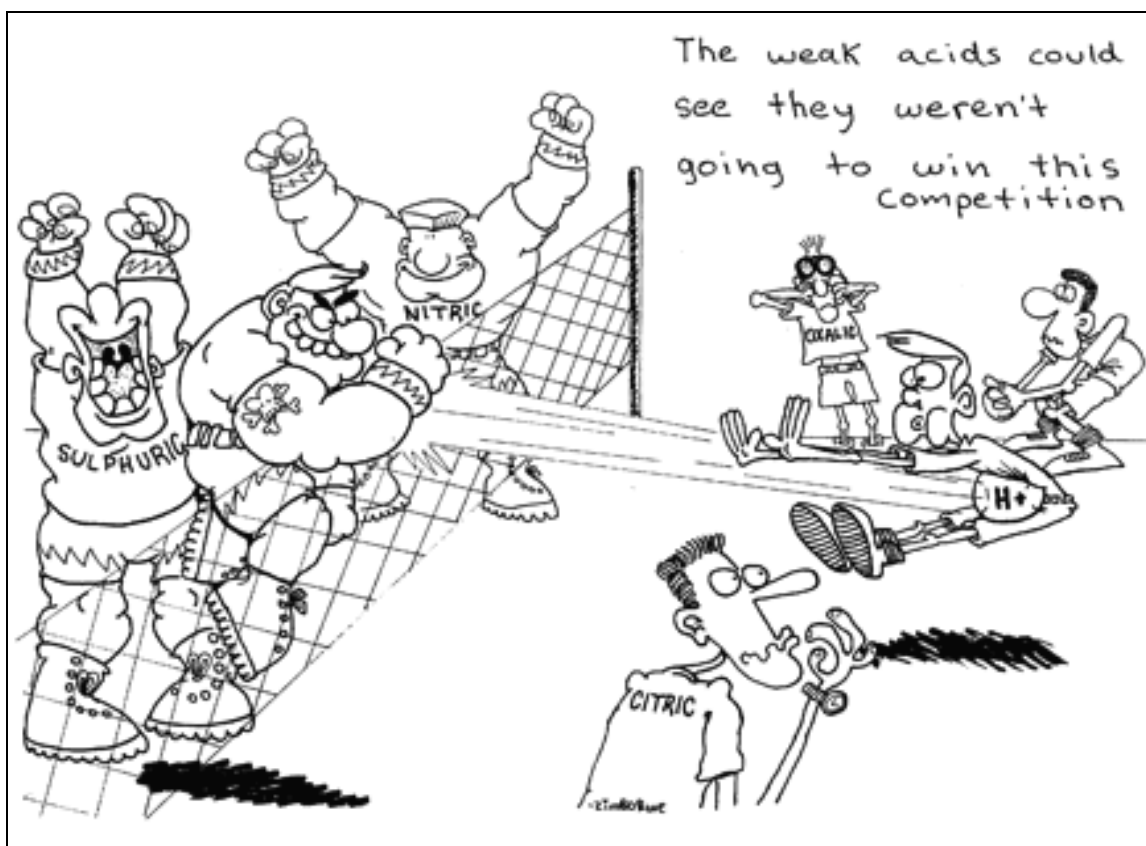


Since  $\text{H}_2\text{S}$  has a greater tendency to donate protons and form its conjugate base,  $\text{HS}^-$ , then there will be more reactants than products when equilibrium is established (reactants are favoured).

Alternately, the equilibrium constant can be calculated for this reaction.

$$K_{\text{eq}} = \frac{K_a(\text{HCO}_3^-)}{K_a(\text{H}_2\text{S})} = \frac{5.6 \times 10^{-11}}{9.1 \times 10^{-8}} = 6.2 \times 10^{-4} = \frac{[\text{products}]}{[\text{reactants}]}$$

Since  $K_{\text{eq}} < 1$ , this agrees with the prediction that there will be more reactants than products.



**EXERCISES:**

38. Write the Brønsted–Lowry acid–base equilibria which occur when the following pairs of substances are mixed in solution. Identify the conjugate pairs formed.

- a)  $\text{HNO}_2$  and  $\text{NH}_3$       c)  $\text{HS}^-$  and  $\text{H}_3\text{PO}_4$       e)  $\text{HCOOH}$  and  $\text{CN}^-$       g)  $\text{HSO}_3^-$  and  $\text{OH}^-$   
 b)  $\text{CO}_3^{2-}$  and  $\text{HF}$       d)  $\text{HCO}_3^-$  and  $\text{S}^{2-}$       f)  $\text{H}_3\text{BO}_3$  and  $\text{HO}_2^-$       h)  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_3$

39. In the following equilibria, predict whether reactants or products are favoured.

- a)  $\text{H}_2\text{S} + \text{NH}_3 \rightleftharpoons \text{HS}^- + \text{NH}_4^+$       d)  $\text{H}_2\text{O}_2 + \text{SO}_3^{2-} \rightleftharpoons \text{HO}_2^- + \text{HSO}_3^-$   
 b)  $\text{H}_2\text{PO}_4^- + \text{HS}^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_2\text{S}$       e)  $\text{CH}_3\text{COOH} + \text{PO}_4^{3-} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{HPO}_4^{2-}$   
 c)  $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$

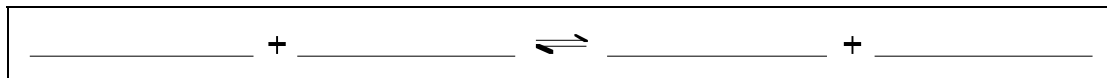
40. Write the major equilibrium reactions which occur when the following substances are put into water. Ignore reactions between the ions and water. All salts are 100% dissociated in water. Do the resulting equilibria favour reactants or products?

- a)  $\text{HSO}_4^-$  and  $\text{NO}_2^-$       e)  $\text{HSO}_3^-$  and  $\text{HC}_2\text{O}_4^-$       h)  $\text{H}_2\text{S}$  and  $\text{NO}_2^-$   
 b)  $\text{H}_3\text{PO}_4$  and  $\text{HPO}_4^{2-}$       f)  $\text{H}_2\text{O}_2$  and  $\text{HS}^-$       i)  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and  $\text{H}_2\text{PO}_4^-$   
 c)  $\text{HCO}_3^-$  and  $\text{HSO}_3^-$       g)  $(\text{NH}_4)_2\text{CO}_3$       j)  $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$  and  $\text{HSO}_3^-$   
 d)  $\text{NH}_4\text{F}$

41.  $K_{\text{eq}} = 14$  for the equilibrium:  $\text{H}_2\text{Te} + \text{HSe}^- \rightleftharpoons \text{HTe}^- + \text{H}_2\text{Se}$ .

- a) Which acid is stronger:  $\text{H}_2\text{Te}$  or  $\text{H}_2\text{Se}$ ?  
 b) Which base is stronger?  
 c) Based on your answers for parts (a) and (b), fill in the blanks in the following using the terms:

**STRONGER ACID, weaker acid, STRONGER BASE and weaker base.**



42. Will  $K_{\text{eq}}$  be greater than or less than 1 for the equilibrium:  $\text{HSO}_4^- + \text{NH}_3 \rightleftharpoons \text{SO}_4^{2-} + \text{NH}_4^+$  ?

43. Consider the following equilibrium which favours **reactants**:  $\text{X}^- + \text{HA} \rightleftharpoons \text{HX} + \text{A}^-$ .

- a) Give the formula of the two bases.  
 b) Which base must be weaker? Why?

44. The following equilibrium favours products:  $\text{Se}^{2-} + \text{HSO}_4^- \rightleftharpoons \text{HSe}^- + \text{SO}_4^{2-}$ .

- a) Which is the stronger of the two acids in the equation?  
 b) If  $\text{NaHSe}$  were added to the solution, how would the above equilibrium be affected?

45. Given:  $\text{HOI} + \text{H}_2\text{GeO}_4^- \rightleftharpoons \text{OI}^- + \text{H}_3\text{GeO}_4$  ;  $K_{\text{eq}} = 8.8 \times 10^{-3}$   
 $\text{HOCl} + \text{OBr}^- \rightleftharpoons \text{OCl}^- + \text{HOBr}$  ;  $K_{\text{eq}} = 14$   
 $\text{HOBr} + \text{H}_2\text{GeO}_4^- \rightleftharpoons \text{OBr}^- + \text{H}_3\text{GeO}_4$  ;  $K_{\text{eq}} = 7.9 \times 10^2$ .

Arrange the four acids involved in order from strongest to weakest.

46. You are given three different acids:  $\text{H}_2\text{SO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HCOOH}$ . Which of these acids would form an equilibrium with  $\text{F}^-$  in which the reactants are favoured? Explain your answer.

## ANSWERS TO UNIT IV : ACIDS AND BASES

---

- (a) Salt  
(b) Acid; this is "acetic acid" and is also written as "CH<sub>3</sub>COOH".  
(c) None; this is an organic covalent compound made from two non-metallic elements .  
(d) Base  
(e) Acid  
(f) Salt  
(g) Base  
(h) None; this is a covalent compound made from two non-metallic elements .
- (a)  $\text{H}_2\text{SO}_4 + 2 \text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O}$                       (d)  $4 \text{HCl} + \text{Sn}(\text{OH})_4 \longrightarrow \text{SnCl}_4 + 4 \text{H}_2\text{O}$   
(b)  $3 \text{H}_2\text{SO}_4 + 2 \text{Fe}(\text{OH})_3 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 6 \text{H}_2\text{O}$                       (e)  $\text{H}_2\text{S} + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaS} + 2 \text{H}_2\text{O}$   
(c)  $\text{H}_3\text{PO}_4 + 3 \text{KOH} \longrightarrow \text{K}_3\text{PO}_4 + 3 \text{H}_2\text{O}$                       (f)  $\text{H}_4\text{P}_2\text{O}_7 + 4 \text{NaOH} \longrightarrow \text{Na}_4\text{P}_2\text{O}_7 + 4 \text{H}_2\text{O}$
- (a) both acids and bases                      (c) bases only                      (e) acids only  
(b) neither acids nor bases                      (d) acids only                      (f) neither acids nor bases
- Use litmus paper: if the litmus is red, you have an acid; if blue, you have a base. If litmus indicates acid is present, add a piece of Mg to some of the solution; bubbles of H<sub>2</sub>(g) should be produced.
- Both NaOH and KOH will absorb H<sub>2</sub>O and CO<sub>2</sub> from the atmosphere, reducing the purity of the bases.
- Fertilizers – H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, NH<sub>3</sub>                      Plastics – H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, NaOH
- (a) H<sub>2</sub>SO<sub>4</sub>                      (b) CH<sub>3</sub>COOH                      (c) NH<sub>3</sub>                      (d) KOH                      (e) HCl
- H<sub>2</sub>SO<sub>4</sub>, NaOH, KOH
- HNO<sub>3</sub>
- (a)  $\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$                       (b)  $\text{HClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$
- (a) acid = HNO<sub>3</sub>, base = H<sub>2</sub>O                      (c) acid = H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, base = HS<sup>-</sup>                      (e) acid = HF, base = CO<sub>3</sub><sup>2-</sup>  
(b) acid = HCO<sub>3</sub><sup>-</sup>, base = SO<sub>3</sub><sup>2-</sup>                      (d) acid = H<sub>3</sub>PO<sub>4</sub>, base = CH<sub>3</sub>COO<sup>-</sup>
- (a) monoprotic = HF, HCN                      (c) triprotic = H<sub>3</sub>PO<sub>4</sub>  
(b) diprotic = H<sub>2</sub>S, H<sub>2</sub>CO<sub>3</sub>                      (d) polyprotic = H<sub>2</sub>S, H<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>
- (a) ACID, BASE, BASE, ACID                      (c) BASE, ACID, BASE, ACID                      (e) ACID, BASE, BASE, ACID  
(b) BASE, ACID, ACID, BASE                      (d) ACID, BASE, ACID, BASE
- HSe<sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, HSO<sub>3</sub><sup>-</sup>
- (a) conjugate acid = CH<sub>3</sub>COOH, conjugate base = CH<sub>3</sub>COO<sup>-</sup>  
(b) conjugate acid = HSO<sub>4</sub><sup>-</sup>, conjugate base = SO<sub>4</sub><sup>2-</sup>  
(c) conjugate acid = PH<sub>4</sub><sup>+</sup>, conjugate base = PH<sub>3</sub>
- (a) SO<sub>4</sub><sup>2-</sup>                      (b) H<sub>2</sub>SO<sub>4</sub>                      (c) O<sup>2-</sup>                      (d) H<sub>2</sub>O
- (a) HF                      (c) HTe<sup>-</sup>                      (e) H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>                      (g) H<sub>2</sub>  
(b) H<sub>2</sub>Te                      (d) CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>                      (f) H<sub>3</sub>PO<sub>3</sub>                      (h) N<sub>2</sub>H<sub>5</sub><sup>+</sup>
- (a) HCO<sub>3</sub><sup>-</sup>                      (c) PO<sub>4</sub><sup>3-</sup>                      (e) N<sub>3</sub><sup>-</sup>                      (g) S<sup>2-</sup>  
(b) C<sub>5</sub>H<sub>5</sub>N                      (d) HO<sub>2</sub><sup>-</sup>                      (f) NO<sub>2</sub><sup>-</sup>                      (h) C<sub>6</sub>H<sub>5</sub>COO<sup>-</sup>

19. (a)  $\text{HCN} + \text{F}^- \rightleftharpoons \text{CN}^- + \text{HF}$  (d)  $\text{HIO}_3 + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{IO}_3^- + \text{HC}_2\text{O}_4^-$   
 (b)  $\text{S}^{2-} + \text{HCOOH} \rightleftharpoons \text{HS}^- + \text{HCOO}^-$  (e)  $\text{NO}_2^- + \text{HSO}_3^- \rightleftharpoons \text{HNO}_2 + \text{SO}_3^{2-}$   
 (c)  $\text{HPO}_4^{2-} + \text{SO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-} + \text{HSO}_4^-$  (f)  $\text{HPO}_4^{2-} + \text{CH}_3\text{COO}^- \rightleftharpoons \text{PO}_4^{3-} + \text{CH}_3\text{COOH}$
20. Measure the conductivity with a "light bulb conductivity tester". If the conductivity is high (that is, the light bulb burns brightly) then the substance has a STRONG ionization (many ions). If the conductivity is low (the light bulb glows, but not very brightly) then the substance has a WEAK ionization (few ions).
21. (a)  $\text{HIO}_3$  (b)  $\text{HSO}_3^-$  (c)  $\text{H}_2\text{PO}_4^-$
22. (a)  $\text{PO}_4^{3-}$  (b)  $\text{HPO}_4^{2-}$  (c)  $\text{OH}^-$  (d)  $\text{HCOO}^-$
23. (a)  $\text{HTe}^-$  and  $\text{HS}^-$  (b)  $\text{HS}^-$  (since its conjugate acid is weaker)
24. (a)  $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$  (d)  $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-$   
 (b)  $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2^- + \text{H}_3\text{O}^+$  (e)  $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$   
 (c)  $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+} + \text{H}_3\text{O}^+$  (f)  $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{H}_2\text{O})_6^{3+} + \text{OH}^-$
25. (a)  $\text{I}^-$  is the conjugate of a strong acid and NEVER acts as a base in aqueous solution. (HI dissociates 100% to form  $\text{H}^+$  and  $\text{I}^-$ , so that  $\text{I}^-$  has ZERO tendency to reform HI.)  
 (b)  $\text{OH}^-$  CAN act as a base (3rd position from bottom, on right-hand side), BUT the equation directly below this equation refers to  $\text{O}^{2-}$  having a 100% tendency to attract  $\text{H}^+$  and form  $\text{OH}^-$ , so that  $\text{OH}^-$  has ZERO tendency to form  $\text{H}^+$  and  $\text{O}^{2-}$  (notice that the reaction arrow points **backwards**). Hence,  $\text{OH}^-$  NEVER acts as an acid in aqueous solution.  
 (c)  $\text{HClO}_4$  and  $\text{HBr}$  are both strong acids, both are 100% dissociated in aqueous solution and both form 1 M solutions of  $\text{H}_3\text{O}^+$  (aq). Hence, both  $\text{HClO}_4$  and  $\text{HBr}$  are the same strength in aqueous solution. ("The levelling effect")
26. HI is a stronger acid than HCl **only when water is absent**. Both HI(aq) and HCl(aq) are 100% dissociated in water, and have the same strength (the "levelling effect"). Since both 0.10 M HI and 0.10 M HCl are dissociated to the same extent, they will produce the same  $[\text{H}_3\text{O}^+]$ : 0.10 M.
27. A low conductivity simply implies that a low concentration of ions is present. Hence, a relatively high concentration of a weak acid (slightly dissociated) can have the same concentration of ions as a dilute solution of a strong acid (100% dissociated).
28.  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$
29. (a)  $[\text{H}_3\text{O}^+]$  increases  
 (b) neutral; the  $[\text{OH}^-]$  increases as the  $[\text{H}_3\text{O}^+]$  increases, so as to keep  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$   
 (c)  $K_w$  increases
30. (a)  $[\text{H}_3\text{O}^+] = 10.0 \text{ M}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-15} \text{ M}$  (c)  $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-4} \text{ M}$ ,  $[\text{OH}^-] = 4.0 \times 10^{-11} \text{ M}$   
 (b)  $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-15} \text{ M}$ ,  $[\text{OH}^-] = 4.0 \text{ M}$  (d)  $[\text{H}_3\text{O}^+] = 8.33 \times 10^{-13} \text{ M}$ ,  $[\text{OH}^-] = 1.20 \times 10^{-2} \text{ M}$
31. (a)  $K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$  (b)  $K_a = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$  (c)  $K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$
32. (a)  $K_b = \frac{[\text{H}_2\text{S}][\text{OH}^-]}{[\text{HS}^-]}$  (b)  $K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$  (c)  $K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$

33. the acid having  $K_a = 1 \times 10^{-5}$   
 34. the base having  $K_b = 7 \times 10^{-6}$   
 35. (a)  $8.3 \times 10^{-13}$  (b)  $7.1 \times 10^{-10}$  (c)  $2.3 \times 10^{-8}$  (d)  $1.6 \times 10^{-7}$  (e)  $6.7 \times 10^{-13}$  (f)  $1.1 \times 10^{-7}$   
 36.  $5.9 \times 10^{-9}$   
 37. Since the problem gives a  $K_b$  value, the substance must be a weak base (even if the substance is amphiprotic it still acts as a weak base rather than a strong base).

38. (a)  $\text{HNO}_2 + \text{NH}_3 \rightleftharpoons \text{NO}_2^- + \text{NH}_4^+$ ; conjugate pairs = ( $\text{HNO}_2$ ,  $\text{NO}_2^-$ ) and ( $\text{NH}_3$ ,  $\text{NH}_4^+$ )  
 (b)  $\text{CO}_3^{2-} + \text{HF} \rightleftharpoons \text{HCO}_3^- + \text{F}^-$ ; conjugate pairs = ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ) and ( $\text{HF}$ ,  $\text{F}^-$ )  
 (c)  $\text{HS}^- + \text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{PO}_4^-$ ; conjugate pairs = ( $\text{HS}^-$ ,  $\text{H}_2\text{S}$ ) and ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ )  
 (d)  $\text{HCO}_3^- + \text{S}^{2-} \rightleftharpoons \text{CO}_3^{2-} + \text{HS}^-$ ; conjugate pairs = ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) and ( $\text{S}^{2-}$ ,  $\text{HS}^-$ )  
 (e)  $\text{HCOOH} + \text{CN}^- \rightleftharpoons \text{HCOO}^- + \text{HCN}$ ; conjugate pairs = ( $\text{HCOOH}$ ,  $\text{HCOO}^-$ ) and ( $\text{CN}^-$ ,  $\text{HCN}$ )  
 (f)  $\text{H}_3\text{BO}_3 + \text{HO}_2^- \rightleftharpoons \text{H}_2\text{BO}_3^- + \text{H}_2\text{O}_2$ ; conjugate pairs = ( $\text{H}_3\text{BO}_3$ ,  $\text{H}_2\text{BO}_3^-$ ) and ( $\text{HO}_2^-$ ,  $\text{H}_2\text{O}_2$ )  
 (g)  $\text{HSO}_3^- + \text{OH}^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}_2\text{O}$ ; conjugate pairs = ( $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ) and ( $\text{OH}^-$ ,  $\text{H}_2\text{O}$ )  
 (h)  $\text{H}_2\text{O} + \text{H}_2\text{SO}_3 \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_3^-$ ; conjugate pairs = ( $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$ ) and ( $\text{H}_2\text{SO}_3$ ,  $\text{HSO}_3^-$ )

39. (a) products ( $\text{H}_2\text{S}$  is a stronger acid than  $\text{NH}_4^+$ )

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{H}_2\text{S})}{K_a(\text{NH}_4^+)} = \frac{9.1 \times 10^{-8}}{5.6 \times 10^{-10}} = 1.6 \times 10^2 = \frac{[\text{products}]}{[\text{reactants}]}$$

and since  $K_{\text{eq}} > 1$  then products are favoured.

- (b) reactants ( $\text{H}_2\text{S}$  is a stronger acid than  $\text{H}_2\text{PO}_4^-$ )

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{H}_2\text{PO}_4^-)}{K_a(\text{H}_2\text{S})} = \frac{6.2 \times 10^{-8}}{9.1 \times 10^{-8}} = 0.68 = \frac{[\text{products}]}{[\text{reactants}]}$$

and since  $K_{\text{eq}} < 1$  then reactants are favoured (barely).

- (c) products ( $\text{NH}_4^+$  is a stronger acid than  $\text{H}_2\text{O}$ )

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{NH}_4^+)}{K_a(\text{H}_2\text{O})} = \frac{5.6 \times 10^{-10}}{1.0 \times 10^{-14}} = 5.6 \times 10^4 = \frac{[\text{products}]}{[\text{reactants}]}$$

and since  $K_{\text{eq}} > 1$  then products are favoured.

- (d) reactants ( $\text{HSO}_3^-$  is a stronger acid than  $\text{H}_2\text{O}_2$ )

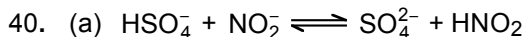
$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{H}_2\text{O}_2)}{K_a(\text{HSO}_3^-)} = \frac{2.4 \times 10^{-12}}{1.0 \times 10^{-7}} = 2.4 \times 10^{-5} = \frac{[\text{products}]}{[\text{reactants}]}$$

and since  $K_{\text{eq}} < 1$  then reactants are favoured.

- (e) products ( $\text{CH}_3\text{COOH}$  is a stronger acid than  $\text{HPO}_4^{2-}$ )

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{CH}_3\text{COOH})}{K_a(\text{HPO}_4^{2-})} = \frac{1.8 \times 10^{-5}}{2.2 \times 10^{-13}} = 8.2 \times 10^7 = \frac{[\text{products}]}{[\text{reactants}]}$$

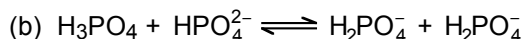
and since  $K_{\text{eq}} > 1$  then products are favoured.



and:  $K_a(\text{HSO}_4^-) > K_a(\text{HNO}_2)$ , so that  $\text{HSO}_4^-$  has a greater tendency to dissociate and products are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{HSO}_4^-)}{K_a(\text{HNO}_2)} = \frac{1.2 \times 10^{-2}}{4.6 \times 10^{-4}} = 26 = \frac{[\text{products}]}{[\text{reactants}]}$$

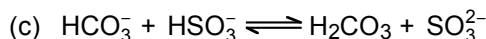
and since  $K_{\text{eq}} > 1$  then products are favoured.



and:  $K_a(\text{H}_3\text{PO}_4) > K_a(\text{H}_2\text{PO}_4^-)$ , so that  $\text{H}_3\text{PO}_4$  has a greater tendency to dissociate and products are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{H}_3\text{PO}_4)}{K_a(\text{H}_2\text{PO}_4^-)} = \frac{7.5 \times 10^{-3}}{6.2 \times 10^{-8}} = 1.2 \times 10^5 = \frac{[\text{products}]}{[\text{reactants}]}$$

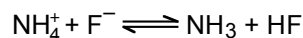
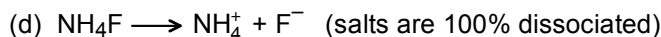
and since  $K_{\text{eq}} > 1$  then products are favoured.



and:  $K_a(\text{HSO}_3^-) < K_a(\text{H}_2\text{CO}_3)$ , so that  $\text{H}_2\text{CO}_3$  has a greater tendency to dissociate and reactants are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{HSO}_3^-)}{K_a(\text{H}_2\text{CO}_3)} = \frac{1.0 \times 10^{-7}}{4.3 \times 10^{-7}} = 0.23 = \frac{[\text{products}]}{[\text{reactants}]}$$

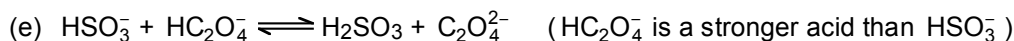
and since  $K_{\text{eq}} < 1$  then reactants are favoured.



and:  $K_a(\text{NH}_4^+) < K_a(\text{HF})$ , so that HF has a greater tendency to dissociate and reactants are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{NH}_4^+)}{K_a(\text{HF})} = \frac{5.6 \times 10^{-10}}{3.5 \times 10^{-4}} = 1.6 \times 10^{-6} = \frac{[\text{products}]}{[\text{reactants}]}$$

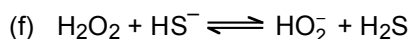
and since  $K_{\text{eq}} < 1$  then reactants are favoured.



and:  $K_a(\text{HC}_2\text{O}_4^-) < K_a(\text{H}_2\text{SO}_3)$ , so that  $\text{H}_2\text{SO}_3$  has a greater tendency to dissociate and reactants are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{HC}_2\text{O}_4^-)}{K_a(\text{H}_2\text{SO}_3)} = \frac{6.4 \times 10^{-5}}{1.5 \times 10^{-2}} = 4.3 \times 10^{-3} = \frac{[\text{products}]}{[\text{reactants}]}$$

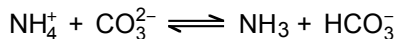
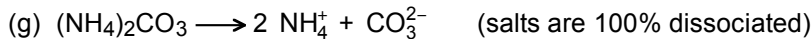
and since  $K_{\text{eq}} < 1$  then reactants are favoured.



and:  $K_a(\text{H}_2\text{O}_2) < K_a(\text{H}_2\text{S})$ , so that  $\text{H}_2\text{S}$  has a greater tendency to dissociate (reactants are favoured).

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{H}_2\text{O}_2)}{K_a(\text{H}_2\text{S})} = \frac{2.4 \times 10^{-12}}{9.1 \times 10^{-8}} = 2.6 \times 10^{-5} = \frac{[\text{products}]}{[\text{reactants}]}$$

and since  $K_{\text{eq}} < 1$  then reactants are favoured.

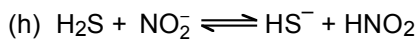


and:  $K_a(\text{NH}_4^+) > K_a(\text{HCO}_3^-)$ , so that  $\text{NH}_4^+$  has a greater tendency to dissociate and products are favoured.

(Note that only one proton is transferred; the fact that  $[\text{NH}_4^+]$  is twice  $[\text{CO}_3^{2-}]$  when  $(\text{NH}_4)_2\text{CO}_3$  dissociates will only push the equilibrium farther to the products side than might otherwise occur if all reactant concentrations were 1 M.)

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{NH}_4^+)}{K_a(\text{HCO}_3^-)} = \frac{5.6 \times 10^{-10}}{5.6 \times 10^{-11}} = 1.0 \times 10^1 = \frac{[\text{products}]}{[\text{reactants}]}$$

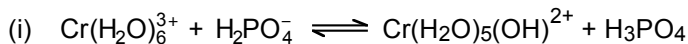
and since  $K_{\text{eq}} > 1$  then products are favoured.



and:  $K_a(\text{H}_2\text{S}) < K_a(\text{HNO}_2)$ , so that  $\text{HNO}_2$  has a greater tendency to dissociate and reactants are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{H}_2\text{S})}{K_a(\text{HNO}_2)} = \frac{9.1 \times 10^{-8}}{4.6 \times 10^{-4}} = 2.0 \times 10^{-4} = \frac{[\text{products}]}{[\text{reactants}]}$$

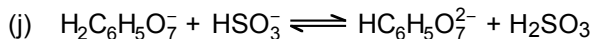
and since  $K_{\text{eq}} < 1$  then reactants are favoured.



and:  $K_a(\text{H}_3\text{PO}_4) > K_a(\text{Cr}(\text{H}_2\text{O})_6^{3+})$ , so that  $\text{H}_3\text{PO}_4$  has a greater tendency to dissociate and reactants are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{Cr}(\text{H}_2\text{O})_6^{3+})}{K_a(\text{H}_3\text{PO}_4)} = \frac{1.5 \times 10^{-4}}{7.5 \times 10^{-3}} = 0.020 = \frac{[\text{products}]}{[\text{reactants}]}$$

and since  $K_{\text{eq}} < 1$  then reactants are favoured.



and:  $K_a(\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-) < K_a(\text{H}_2\text{SO}_3)$ , so that  $\text{H}_2\text{SO}_3$  has a greater tendency to dissociate and reactants are favoured.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-)}{K_a(\text{H}_2\text{SO}_3)} = \frac{1.7 \times 10^{-5}}{1.5 \times 10^{-2}} = 1.1 \times 10^{-3} = \frac{[\text{products}]}{[\text{reactants}]}$$

and since  $K_{\text{eq}} < 1$  then reactants are favoured.

41. (a)  $\text{H}_2\text{Te}$  (b)  $\text{HSe}^-$  (c) STRONGER ACID + STRONGER BASE  $\rightleftharpoons$  weaker base + weaker acid

42. greater than 1 since  $\text{HSO}_4^-$  is a stronger acid than  $\text{NH}_4^+$  and forces the equilibrium to the products side.

$$\text{or: } K_{\text{eq}} = \frac{K_a(\text{HSO}_4^-)}{K_a(\text{NH}_4^+)} = \frac{1.2 \times 10^{-2}}{5.6 \times 10^{-10}} = 2.1 \times 10^7 > 1.$$

43. (a)  $\text{X}^-$  and  $\text{A}^-$  (b)  $\text{X}^-$  is weaker; if reactants are favoured, then  $\text{HX}$  is stronger than  $\text{HA}$ . Since the stronger the acid, the weaker its conjugate base, then  $\text{X}^-$  is weaker.

44. (a)  $\text{HSO}_4^-$  is stronger than  $\text{HSe}^-$

(b)  $\text{NaHSe} \longrightarrow \text{Na}^+ + \text{HSe}^-$ ; the added  $\text{HSe}^-$  shifts the equilibrium more to the reactants side.

45.  $\text{HOCl} > \text{HOBr} > \text{H}_3\text{GeO}_4 > \text{HOI}$