PRACTICAL NUMBER 9
ACID STRENGTH AND STRUCTURE

INTRODUCTION

In this exercise you will compare the strengths of several acids and, as far as possible, relate the strength of each acid to its structure and bonding. As a consequence some general principles may emerge which will assist you to understand some of the factors that determine the strength of an acid.

Consider two different acids HA and HB. These hydrolyse in aqueous solution as follows:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(l) + A^-(aq) \tag{9.1}$$

$$HB(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B^-(aq) \tag{9.2}$$

Their strengths are described by the value of the equilibrium constant, K_a, and hence by the position of equilibrium under comparable conditions. The larger the value of K_a, the stronger the acid, and the further equilibrium lies to the right. As a consequence, if a 0.1 M solution of HA has a higher concentration of H_3O^+, and so a lower pH, than a 0.1 M solution of HB then HA is a stronger acid than HB.

Alternatively consider the bases A^- and B^-. These are the conjugate bases of HA and HB respectively. In aqueous solution they hydrolyse as follows:

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \tag{9.3}$$

$$B^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HB(aq) \tag{9.4}$$

The base strength is described by the value of the equilibrium constant K_b: the higher the value of K_b, the stronger the base. Under comparable conditions the equilibrium position lies further to the left for the weaker base. This means that the concentration of OH^- is lower, and hence if a 0.1 M solution of A^- has a lower pH than a 0.1 M solution of B^-, then A^- is a weaker base than B^-. Since the K_a and K_b values of a conjugate pair are related by:

$$K_a \times K_b = K_w \tag{9.5}$$

and K_w is a constant, the smaller the value of K_b, the larger the value of K_a. This means that for the conjugate acids HA and HB, HA is the stronger acid when the solution of A^- has the lower pH.

The question then arises, "Why is HA a stronger acid than HB?" Acid strength is a consequence of the interplay of many factors. Some of these factors can be identified if the acid strengths of similar molecules are compared. It is necessary to consider the nature of the bonding of the hydrogen atom to the rest of the molecule (or ion). Factors which affect the strength and polarity of the bond to hydrogen[14] in an acid have an important influence on acid strength. For this purpose acids may be classified under five different headings: *non-metal hydrides, oxoacids, carboxylic acids, aquocations* and *polyprotic acids*. For each type, there are rules which are a good guide to the relative strengths of these acids, and hence of their conjugate bases (see equation 9.5).
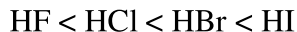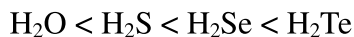
1) Non-metal hydrides

These may also be referred to as *binary acids*, and are compounds of a given element with hydrogen only. Hydrides of electronegative elements are, at least in principle, weakly acidic. Proceeding from left to right across a period the non-metal hydrides increase in acid strength:

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[14] Do not use the term *hydrogen bond* in this context: it applies to a weak non-bonding interaction, an intermolecular force, not a bond as such.

$CH_4 < NH_3 < H_2O < HF$
$SiH_4 < PH_3 < H_2S < HCl$
extremely   much
weak   stronger
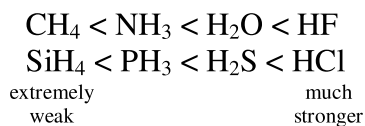
(HCl is strong, whereas HF is weak.) This effect may be ascribed to the increasing electronegativity of elements across a period. Electronegative atoms withdraw electrons from the bond with hydrogen, making it weaker. Tables of electronegativities are to be found in most general chemistry textbooks.

Unfortunately this pattern does not hold as we pass down a group. The order of acid strength is the reverse of what we would expect on the basis of the above argument, since electronegativity decreases but acid strength increases. Thus we have for the group VI and VII hydrides:

$H_2O < H_2S < H_2Se < H_2Te$

$HF < HCl < HBr < HI$

A similar trend is noted for the group V hydrides, but none of the group IV hydrides is appreciably acidic.

The determining factor here is the strength of the bond between the non-metal atom and the hydrogen atom. This decreases rapidly as the size of the non-metal atom increases. Since the size of an atom increases going down a group, the acid strength increases.

2)   Oxoacids

These are acids whose molecules contain hydrogen, oxygen, and one other element. Acidic hydrogens are bonded to oxygen. Their formulae can be represented as $XO_m(OH)_n$. For example H_3PO_4 can be represented as $PO(OH)_3$, that is,
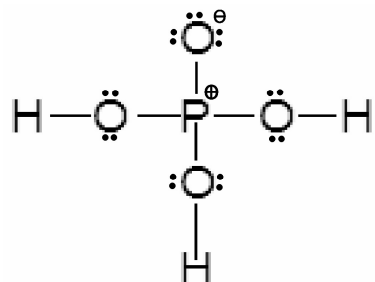
Here X is phosphorus, m = 1 and n = 3.

The value of n (i.e. number of hydroxyl groups bonded to the central atom) is not important in deciding the strength of the acid. The important factors are the value of m (i.e. number of oxygen atoms not bonded to hydrogen) and the electronegativity of the central atom, X, with the value of m being the most important factor[15].

a)   Value of m in the general formula $XO_m(OH)_n$

The acid strength increases rapidly as m increases. For example:

Name of acid	Usual formula	Modified formula	Value of m	pK$_a$ value
hypochlorous	HClO	Cl(OH)	0	7.2
chlorous	HClO$_2$	ClO(OH)	1	2.0

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[15] These rules are known as *Pauling's Rules.*

| chloric | $HClO_3$ | $ClO_2(OH)$ | 2 | -2.7 |
| perchloric | $HClO_4$ | $ClO_3(OH)$ | 3 | -10 |

Note that a smaller, or more negative value of pK_a, implies a larger value of K_a and hence a stronger acid.
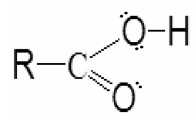
b) *Electronegativity of central atom*

The more electronegative the atom X, the stronger the acid. Thus:

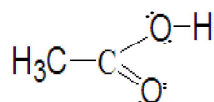| *Name of acid*	*Usual formula*	*Modified formula*	*Electronegativity of X*	*pK_a value*
hypochlorous	HClO	Cl(OH)	3.0	7.2
hypobromous	HBrO	Br(OH)	2.8	8.7
hypoiodous	HIO	I(OH)	2.5	10.0

3) *Carboxylic acids*

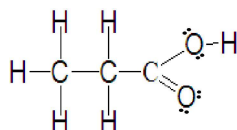These are organic acids possessing the grouping:

where R represents a hydrocarbon chain, or similar. Only the hydrogen bonded to O is acidic.
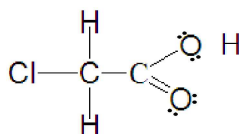
For example, ethanoic acid (CH_3CO_2H) is:

and propanoic acid ($CH_3CH_2CO_2H$) is:

It is possible to replace one or more of the hydrogens with chlorine atoms, e.g. chloroethanoic acid is:

Since chlorine is electronegative it tends to withdraw electrons from the rest of the molecule, including the O-H bond, making it weaker, and therefore making chloroethanoic acid a stronger acid than ethanoic acid (pK_a = 2.86 and 4.76 respectively). Similarly, dichloroethanoic acid ($CHCl_2CO_2H$) is stronger still, with pK_a = 1.26, since there are two chlorine atoms, both pulling electrons away from the O-H bond. Trichloroethanoic acid is a strong acid, pK_a = 0.64.

Fluorine has a greater effect than chlorine, since it is more electronegative than chlorine. The pK_a of fluoroethanoic acid is 2.59.

If the electronegative atom is more distant from the carboxylic acid group, as in 3-chloropropanoic acid, $CH_2ClCH_2CO_2H$, the effect is somewhat less pronounced. Thus pK_a for propanoic acid is 4.87, as

against $pK_a = 4.00$ for 3-chloropropanoic acid.

Note that propanoic acid is a weaker acid than ethanoic acid. This is because propanoic acid can be regarded as being derived from ethanoic acid by replacing a hydrogen atom by a $-CH_3$ group. Since the $-CH_3$ group is (effectively) more electropositive than hydrogen, it actually donates electrons to the C-H bond, and makes it stronger. The larger the hydrocarbon group attached to the carboxylic acid group, the weaker will be the acid. Thus 3,3-dimethylpropanoic acid $(CH_3)_3CCO_2H$ has $pK_a = 5.05$.

4)   Aquocations

All metal ions are surrounded by a cage of more or less tightly bound water molecules when they are in aqueous solution. The whole assembly is an *aquocomplex*. Generally there are either four or six of the most tightly bound, and therefore closest, of these molecules. For example, the iron(III) cation in aqueous solution can be written as $[Fe(H_2O)_6]^{3+}$ and drawn as
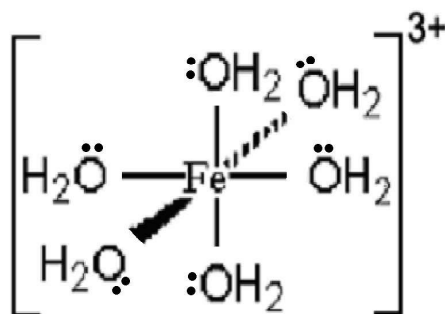
The positive charge on the metal ion attracts the negative ends (oxygen atoms) of the water molecules. It therefore also attracts electrons from the O-H bonds in the water molecules, weakening these bonds. These hydrogen atoms become appreciably acidic. $[Fe(H_2O)_6]^{3+}$ dissociates in successive stages of which the first is:

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq) \qquad (9.6)$$

(See polyprotic acids below.)

The acidity of the aquocomplex is decided by the polarising power of the metal atom. This is greater for smaller, more highly charged metal ions, such as Fe^{3+} and Al^{3+}. The important parameter is the **charge/radius ratio**, which is given, in relative terms, by the charge divided by the radius of the metal ion. Most textbooks have tables of atomic radii.

In addition, the presence of an appreciable amount of dative covalent bonding between the metal ion and the water molecules enhances the effect. Transition metal ions are usually good at forming these dative covalent bonds. Thus solutions of copper(II) ions (containing $[Cu(H_2O)_4]^{2+}$) are more acidic than might be expected from the size and charge of the copper(II) ion.

5)   Polyprotic acids

If an acid contains more than one hydrogen atom which can be lost (as a hydrogen ion) it is a polyprotic (or polybasic) acid. Not all hydrogen atoms in a molecule are acidic. Thus ethanoic acid (see section 3 above) is a monoprotic acid, despite the fact that it contains 4 hydrogen atoms in each molecule.

The first hydrogen atom is always the easiest to remove. As a hydrogen ion, H^+, is removed, the original neutral molecule turns into a negative ion. The negative charge makes it more difficult for the hydrogen ion to depart. When a second hydrogen ion is removed it is departing from a doubly charged ion, which attracts it even more strongly. The effect is even more pronounced for the loss of a third hydrogen ion.

Thus the pK_a values for phosphoric acid (H_3PO_4) are 2.15, 7.20 and 12.38 for the removal of the first, second and third hydrogen ions respectively. In general the pK_a values for small molecules like this tend to increase by about five between successive hydrogens. In other words the K_a values decrease by about 5 orders of magnitude each time. The effect is not so pronounced for molecules such as citric acid:
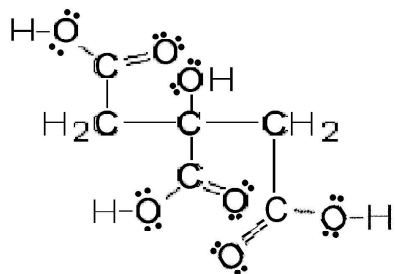
where the acidic hydrogens are further apart from one another in the molecule. The pK_a values for citric acid are 3.13, 4.76 and 6.40 respectively.

METHOD

First determine the pH of the distilled water available in the laboratory. Note that water from different containers may have rather different pH values as a result of the various impurities present.

Determine the pH of the solutions listed in Results Table 9.1 by testing them with pH paper or with a pH meter. If you use pH paper, try a broad range paper first, and then use a narrow range paper (if one is available) to determine the pH more accurately. Note the pH value and then write the hydrolysis reaction in any instance where the pH differs appreciably from that of the water used.

Refer now to Results Table 9.2 and, on the basis of your results recorded in Results Table 9.1, decided which of the acids in each pair is the stronger, draw valence bond structures for the acids and advance an explanation of the differences in acid strength. Show all lone pairs and formal charges. Bonding pairs may be indicated by dashes. Note that the same explanation applies to two pairs at a time.

RESULTS

Table 9.1

Solution	pH	Hydrolysis reaction (if any)
H_2O		
0.1 M NaF		
0.1 M NaCl		
0.1 M H_2S		
0.1 M H_2SO_4		
0.1 M H_3PO_4		

Solution	pH	Hydrolysis reaction (if any)
0.1 M NaHSO$_4$		
0.1 M NaH$_2$PO$_4$		
0.1 M NaHSO$_3$		
0.1 M NaNO$_3$		
0.1 M NaNO$_2$		
0.1 M CH$_3$CO$_2$H		
0.1 M CH$_2$ClCO$_2$H		
0.1 M CCl$_3$CO$_2$H		
0.1 M Al(NO$_3$)$_3$		
0.1 M Mg(NO$_3$)$_2$		

Note: In the following table the acids are arranged in pairs. The explanation for the difference in strength between the first pair of acids, for example, is the same as the explanation for the difference in strength for the second pair. Thus only one space for explanation is left for these four acids. The next four follow the same pattern, and so on.

Table 9.2

Pairs of acids (tick stronger one)	Valence bond structure of acids	Explanation of difference in strength
HF HCl		
H$_2$O H$_2$S		

H_2SO_4 H_3PO_4		
HSO_4^- $H_2PO_4^-$		
H_2SO_4 HSO_4^-		
H_3PO_4 $H_2PO_4^-$		
H_2SO_4 H_2SO_3		
HNO_3 HNO_2		
CH_3CO_2H CH_2ClCO_2H		
CH_2ClCO_2H CCl_3CO_2H		
$[Al(H_2O)_6]^{3+}$ $[Mg(H_2O)_6]^{2+}$		
$[Mg(H_2O)_6]^{2+}$ $[Na(H_2O)_6]^+$		

PROBLEMS

Consider the following pairs of acids. Carefully explain which one of each pair is the stronger, and why.

1)   HOCl   HOClO

2) $HClO_3$ HIO_3

3) H_2S H_2Se

4) $CH_3CHClCO_2H$ $CH_2ClCH_2CO_2H$

5) $[Mg(H_2O)_6]^{2+}$ $[Ca(H_2O)_6]^{2+}$

6) $[Fe(H_2O)_6]^{2+}$ $[Fe(H_2O)_6]^{3+}$