Chem Factsheet

January 2002 Number 25

Acid-Base Equilibria I - pH, K_w and K_a

To succeed in this topic you need to be able to:

- **understand the writing of K_c expressions and their units (covered in Factsheet No.21);**
- **use your calculator to convert numbers into 'logarithms to the base 10 ($\log_{10}$) using the [lg] key;**
- **turn $\log_{10}$ values back into numbers using the inverse of $\log_{10}$ i.e. the [10^x] key (or second function above the [lg] key).**

After working through this Factsheet you will be able to:

- **use the A2 level definitions of acids and bases (Brønsted-Lowry theory) and identify conjugate acid/base pairs;**
- **define pH and perform calculations using its mathematical expression;**
- **understand how to use the ionic product of water, K_w, to calculate the pH of a base;**
- **understand the difference between the terms weak, strong, concentrated and dilute as applied to acids and bases;**
- **write K_a expressions for weak acids and perform calculations using these expressions.**

> ***Exam Hint***:- *Questions tend to be based on:*
> - *learning the definitions for acids/bases, pH, pOH, K_w and K_a*
> - *performing calculations on them*
>
> *The calculations all involve using the lg and 10^x keys on the calculator **and** being able to input 'powers to the 10' e.g. 1.2×10^{-3}, 5×10^{-6} - this usually involves using the EXP key - eg 1.3 EXP -2 = 1.3×10^{-2} (be careful where you put the minus!)*
>
> ** Many marks are lost in examination questions on this topic by candidates who cannot use their calculators for these purposes. you **must** practice this until you are competent!**

Brønsted-Lowry Theory

At GCSE level you were taught that acids needed water to be present to show their acidic properties, and that they produced H^+ ions. The Brønsted-Lowry Theory takes this one step further:

> ***Acids** are species that **donate** protons/H^+*
> ***Bases** are species that **accept** protons/H^+*

Monobasic acids (e.g. HCl, HNO_3) donate one H^+, dibasic acids (e.g. H_2SO_4) donate two H^+ and tribasic acids (e.g. H_3PO_4) donate three H^+

Acids and bases are linked by the H^+ as this example shows:-

$$HCl \rightarrow H^+ + Cl^-$$

acid conjugate base

The HCl and Cl^- are a **conjugate acid/base pair.**

Note that this new definition of bases includes species such as Cl^- that would not have been regarded as bases at GCSE, and do not show basic character.

Generally, the conjugate base of a weak acid will show weak basic character, whilst the conjugate base of a strong acid will not show basic character.

Usually there are **two acid/base pairs:**

e.g. $HCl + NH_3 \rightarrow NH_4^+ + Cl^-$

acid 1 base 2 acid 2 base 1

e.g. $H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$

acid 1 base 2 acid 2 base 1

This is 'chase the H^+' because it is not seen as a separate entity in the equation although it is being donated and accepted.

The 1 and 2 used have no significance except to identify which acid goes with which base.

For practice on conjugate acid-base pairs go to question 1.

Using acid and base terms

Strong - acid or base which undergoes 100% dissociation as shown by $\rightarrow$

e.g. $HNO_3 \rightarrow H^+ + NO_3^-$
$NaOH \rightarrow Na^+ + OH^-$

N.B. At A2 level there are only
four strong acids: HCl, HNO_3, H_2SO_4 and H_3PO_4
two strong bases: NaOH and KOH

Weak - acid or base that only partially dissociates so it has the equilibrium sign

e.g. $CH_3COOH \quad CH_3COO^- + H^+$
$NH_4OH \quad NH_4^+ + OH^-$

N.B. At A2 level organic acids e.g. methonoic, ethonoic, proponoic, etc are weak, but NH_3(aq) / NH_4OH is the only weak base.

Concentrated/dilute

These terms refer to the ratio of moles to volume i.e. mol dm^{-3} of the solutions of acid and bases,

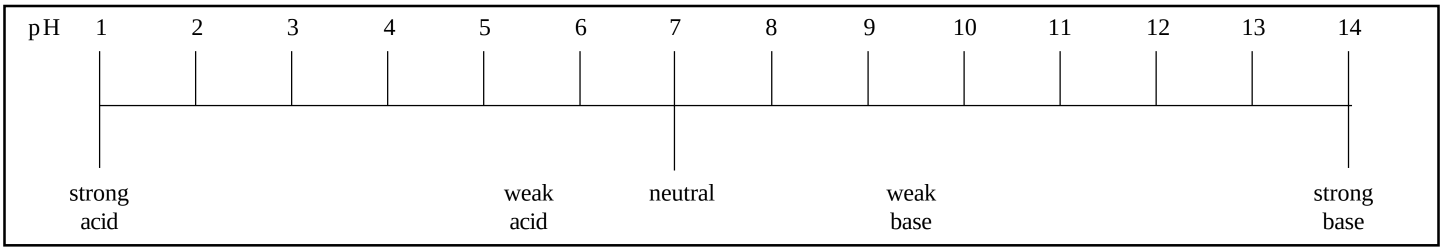
i.e. 2 mol dm^{-3} (2M) would be considered 'dilute' and 6 mol dm^{-3} (6M) 'concentrated'.

There is no 'cut-off' value between 'dilute' and 'concentrated' as descriptions of acids and alkalis – and it will not give you any problems.

So it is possible to have a concentrated weak acid and a dilute strong acid.

pH
You will know the term pH from the 'pH scale' and its link to Universal Indicator colours (Fig 1).

Fig 1. pH scale



At A2 level the numbers 1 – 14 are a logarithmic scale linked to the mathematical expression below.

> ***Definition of pH***
> *pH is the minus log to the base 10 of the hydrogen ion concentration.*
>
> $$pH = -\log_{10}[H^+]$$

For practice on pH and $[H^+]$ calculations using the calculator (lg and 10^x keys) go to question 2 and 3.

> **What are logs (or logarithms)?**
> Logs are related to powers:
> $\log_{10}100 = \log_{10}10^2 = 2$
> $\log_{10}0.1 = \log_{10}10^{-1} = -1$
> So if $\log_{10}(0.63) = -0.201$, then $0.63 = 10^{-0.201}$
>
> On your calculator, the key for "$\log_{10}$" will be called "log" or "lg"

The pH of strong acids
Strong acids undergo 100% dissociation so the concentration (mol dm^{-3} or molarity, M) is all that is needed to calculate its pH.

e.g. Q. What is the pH of 0.1 mol dm^{-3} HCl ?

A.
$$HCl \rightarrow H^+ + Cl^-$$
$$0.1 \rightarrow 0.1 + 0.1$$
$$pH = -\log_{10}[H^+] = -\log_{10}[0.1]$$
$$\therefore \mathbf{pH = 1}$$

e.g. Q. What is the pH of 0.05 mol dm^{-3} H_2SO_4 ?

A.
$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$
$$0.05 \rightarrow 0.1 + 0.05$$
$$pH = -\log_{10}[H^+] = -\log_{10}[0.1]$$
$$\therefore \mathbf{pH = 1}$$

The ionic product of water, K_w
Water partially ionises, H_2O $H^+ + OH^-$

Writing the K_c expression $K_c = \dfrac{[H^+] \times [OH^-]}{[H_2O]}$

We can rearrange this to give:
$$K_c \times [H_2O] = [H^+] \times [OH^-]$$

Since $[H_2O]$ is very large it can be considered a constant, we define:
$$K_w = [H^+] \times [OH^-]$$ *(the w stands for water)*

This gives us $K_c \times [H_2O] = K_w$

At 25°C, $K_w = 10^{-14}$ mol dm^{-3}

Notice that if $[H^+] = [OH^-]$ the solution is **neutral,** then:
$[H]^2 = K_w = 10^{-14}$, so $[H] = \sqrt{10^{-14}} = 10^{-7}$
$\therefore$ pH $= -\log_{10}(10^{-7}) = 7$

You will see the link between 'neutral' and a pH of 7 (although this is only true at 25°C - at higher temperatures K_w increases, and so does the pH of water.)

The reason K_w is introduced to be able to calculate the pH of bases which lie in the range of pH 8 – 14 at 25°C

e.g. Q. What is the pH of 0.1 mol dm^{-3} NaOH?

A.
$$NaOH \rightarrow Na^+ + OH^-$$
$$0.1 \rightarrow 0.1 + 0.1$$
$$K_w = [H^+] \times [OH^-] = 10^{-14}$$
$$[H^+] \times 0.1 = 10^{-14}$$
$$[H^+] = \frac{10^{-14}}{0.1} = 10^{-13}$$
$$pH = -\log_{10}[H^+] = -\log_{10}[10^{-13}]$$
$$\therefore \mathbf{pH = 13}$$

For further practice on calculations involving pH of strong bases go to question 4.

The pH of weak acids and K_a
A **weak** acid only partially dissociates, so the concentration of hydrogen ions, $[H^+]$ cannot be calculated from the concentration, mol dm^{-3}, as it can for strong acids.

Since a weak acid only partially dissociates there is an equilibrium set up:

$$HA \quad H^+ + A^-$$

and you can write the K_c expression,

$$K_c = \frac{[H^+] \times [A^-]}{[HA]}$$

For acids, we use K_a (where a = acid) instead of K_c

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

Note that K_a is **not defined** for **strong acids**, because there will be no undissociated acid left.

Since $1\,HA \rightarrow 1\,H^+ + 1\,A^-$ every time HA dissociates (according to the moles in the equation):
$$[H^+] = [A^-]$$

If the degree of dissociation is very small (which is the case for weak acids) then $[H^+]$ is very small compared to [HA]. This means we can use:
$[HA] - [H^+] \approx [HA]$
i.e. we can assume that the concentration of [HA] remains at its original value.

The equation now becomes,

$$\boxed{K_a = \frac{[H^+]^2}{[HA]}}$$

Units = mol dm^{-3}

The two types of calculation, using the equation are now:

1. Finding K_a - given pH and concentration of the acid.	
Method	Q. 0.1 mol dm^{-3} solution of HA has a pH of 5.10. What is its K_a value?
(1) Calculate the [H$^+$] from the pH value	A. pH = - log$_{10}$ [H$^+$] 5.10 = - log$_{10}$ [H$^+$] [H$^+$] = $10^{-5.10}$ = 7.94×10^{-6}
(2) Use the K_a expression where [H$^+$] = [A$^-$]	$K_a = \frac{[H^+]^2}{[HA]}$
(3) Substitute the values for [H$^+$] and [HA]	$K_a = \frac{(7.94 \times 10^{-6})^2}{0.1}$
(4) Calculate the answer and give **units**.	= **6.3×10^{-10} mol dm^{-3}**
2. Finding pH - given K_a and the concentration of the acid.	
Method	Q. 0.1 mol dm^{-3} CH_3CO_2H has a $K_a = 1.7 \times 10^{-5}$ mol dm^{-3}. What is its pH?
(1) Write the K_a expression for the acid given i.e. CH_3CO_2H	A. $K_a = \frac{[H^+]^2}{[CH_3COOH]}$
(2) Substitute in the values for K_a and acid concentration	$1.7 \times 10^{-5} = \frac{[H^+]^2}{0.1}$
(3) Calculate the [H$^+$] value	[H$^+$] = $\sqrt{1.7 \times 10^{-5} \times 0.1}$ = 1.3×10^{-3} mol dm^{-3}
(4) Substitute into the pH expression and calculate the answer.	pH = -log$_{10}$ [H$^+$] = -log$_{10}$ (1.3×10^{-3}) = 2.9

For further practice on K_a calculations go to question 5 and 6

Questions

1. Identify and label the two conjugate acid/base pairs in the following reactions:
   a) $NH_3 + H_2O$ $NH_4^+ + OH^-$
   b) $H_2O + HCl \rightarrow H_3O^+ + Cl^-$
   c) $HNO_3 + OH^- \rightarrow NO_3^- + H_2O$
   d) $H_2O + H_2O$ $H_3O^+ + OH^-$
   e) $HSO_3^- + H_2O \rightarrow H_3O^+ + SO_3^{2-}$

2. What is th pH of solutions with the following [H$^+$] in mol dm^{-3}?
   a) 10^{-7} b) 10^{-4} c) 10^{-3} d) 0.25
   e) 2.0×10^{-5} f) 4.5×10^{-8} g) 7.0×10^{-4} h) 7.9×10^{-2}
   i) 3.2×10^{-6} j) 6.4×10^{-7}

3. What is the [H$^+$] in mol dm^{-3} for the following pH values?
   a) 4 b) 6 c) 11.3 d) 2.7
   e) 6.9 f) 13.1 g) 7.4 h) 1.5
   i) 12.8 j) 3.4

4. What is the pH of strong bases with the following [H$^+$] in mol dm^{-3}?
   a) 10^{-5} b) 10^{-3} c) 0.035 d) 5.4×10^{-9}
   e) 9.9×10^{-2} f) 7.1×10^{-7}

5. Calculate the K_a of the following weak acids:
   a) pH = 3.40 [HA] = 0.010 mol dm^{-3}
   b) pH = 2.40 [HA] = 0.10 mol dm^{-3}
   c) pH = 4.03 [HA] = 0.10 mol dm^{-3}
   d) pH = 4.00 [HA] = 0.10 mol dm^{-3}
   e) pH = 5.70 [HA] = 0.885 mol dm^{-3}

6. What is the pH of the following weak acids?
   a) $K_a = 3.7 \times 10^{-8}$ mol dm^{-3} [HA] = 0.01 mol dm^{-3}
   b) $K_a = 5.8 \times 10^{-10}$ mol dm^{-3} [HA] = 0.01 mol dm^{-3}
   c) $K_a = 5.6 \times 10^{-4}$ mol dm^{-3} [HA] = 0.01 mol dm^{-3}
   d) $K_a = 1.74 \times 10^{-5}$ mol dm^{-3} [HA] = 0.10 mol dm^{-3}
   e) $K_a = 5.62 \times 10^{-4}$ mol dm^{-3} [HA] = 0.20 mol dm^{-3}

Answers

1. a) base 1 + acid 2 acid 1 + base 2
   b) base 1 + acid 2 $\rightarrow$ acid 1 + base 2
   c) acid 1 + base 2 $\rightarrow$ base 1 + acid 2
   d) acid 2 + base 1 acid 1 + base 2
   or base 1 + acid 2
   e) acid 1 + base 2 $\rightarrow$ acid 2 + base 1

2. a) 7 b) 4 c) 3 d) 0.6 e) 4.7
   f) 7.35 g) 3.15 h) 1.1 i) 5.49 j) 6.19

3. a) 10^{-4} b) 10^{-6} c) 5.01×10^{-12} d) 1.99×10^{-3}
   e) 1.25×10^{-7} f) 7.9×10^{-14} g) 3.9×10^{-8} h) 3.16×10^{-2}
   i) 1.58×10^{-13} j) 3.98×10^{-4}

4. a) 9 b) 11 c) 12.5 d) 5.7 e) 13.0
   f) 7.8

5. a) 1.65×10^{-5} b) 1.65×10^{-4} c) 8.7×10^{-8} d) 1×10^{-7}
   e) 4.5×10^{-12}

6. a) 4.72 b) 5.62 c) 2.68 d) 2.88 e) 1.97

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