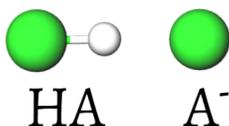


14.7: Conjugate Acid-Base Pairs and pH

One of the more useful aspects of the Brønsted-Lowry definition of acids and bases in helping us deal with the pH of solutions is the concept of the conjugate acid-base pair. We argued qualitatively in [the section on conjugate acid-base pairs in aqueous reactions](#) that the strength of an acid and its conjugate base are inversely related. The stronger one is, the weaker the other will be. This relationship can be expressed quantitatively in terms of a very simple mathematical equation involving the appropriate acid and base constants.

Suppose in the general case we have a weak acid HA whose conjugate base is A^- . If either or both of these species are dissolved in H_2O we will have *both* the following equilibria set up simultaneously.



To the first of these equilibria we can apply the equilibrium constant $K_a(\text{HA})$:

$$K_a(\text{HA}) = \frac{[H_3O^+][A^-]}{[HA]}$$

while to the second we can apply the equilibrium constant $K_b(A^-)$:

$$K_b(A^-) = \frac{[HA][OH^-]}{[A^-]}$$

Multiplying these two constants together, we obtain a simple relationship between them.

$$K_a(\text{HA}) \times K_b(A^-) = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} \quad (14.7.1)$$

$$(14.7.2)$$

$$= [H_3O^+][OH^-] \quad (14.7.3)$$

$$K_a(\text{HA}) \times K_b(A^-) = K_w \quad (14.7.4)$$

If we divide both sides of this equation by the units and take negative logarithms of both sides, we obtain

$$pK_a = -\log \frac{K_a(\text{HA})}{\text{mol L}^{-1}} - \log \frac{K_b(A^-)}{\text{mol L}^{-1}} \quad (14.7.5)$$

$$(14.7.6)$$

$$= -\log \frac{10^{-14} \text{ mol}^2 \text{ L}^{-2}}{\text{mol}^2 \text{ L}^{-2}} \quad (14.7.7)$$

$$pK_a(\text{HA}) + pK_b(A^-) = pK_w \quad (14.7.8)$$

Thus the product of the acid constant for a weak acid and the base constant for the conjugate base must be K_w , and the sum of pK_a and pK_b for a conjugate acid-base pair is 14.

Equation [14.7.4](#) or [14.7.8](#) enables us to calculate the base constant of a conjugate base from the acid constant of the acid, and vice versa. Given the acid constant for a weak acid like HOCl, for instance, we are able to calculate not only the pH of HOCl solutions but also the pH of solutions of salts like NaOCl or KOCl which are, in effect, solutions of the conjugate base of HOCl, namely, the hypochlorite ion, OCl^- .

✓ Example 14.7.1: pH Calculations with K_a

Find the pH of (a) 0.1 M HOCl (hypochlorous acid) and (b) 0.1 M NaOCl (sodium hypochlorite) from the value for K_a given in the [table of \$K_a\$ values](#).

Solution

a) For 0.1 M HOCl, we find in the usual way that

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c_a} \quad (14.7.9)$$

$$= \sqrt{3.1 \times 10^{-8} \text{ mol L}^{-1} \times 0.1 \text{ mol}^2 \text{ L}^{-2}} \quad (14.7.10)$$

$$= 5.57 \times 10^{-5} \text{ mol L}^{-1} \quad (14.7.11)$$

so that pH = 4.25

b) For 0.1 M NaOCl we must first calculate K_b :

$$K_b(\text{OCl}^-) = \frac{K_w}{K_a(\text{HOCl})} \quad (14.7.12)$$

$$= \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{3.1 \times 10^{-8} \text{ mol L}^{-1}} \quad (14.7.13)$$

$$= 3.22 \times 10^{-7} \text{ mol L}^{-1} \quad (14.7.14)$$

Thus

$$[\text{OH}^-] = \sqrt{K_b c_b} \quad (14.7.15)$$

$$= \sqrt{3.22 \times 10^{-7} \times 0.1 \text{ mol}^2 \text{ L}^{-1}} \quad (14.7.16)$$

$$= 1.79 \times 10^{-4} \text{ mol L}^{-1} \quad (14.7.17)$$

From which

$$\text{pOH} = 3.75$$

$$\text{and pH} = 14.00 - \text{pOH} = 10.25$$

In this, as in all pH problems, it is worth checking that the answers obtained are not wildly unreasonable. A pH of 4 for a weak acid is reasonable, though a little high, but then HOCl is among the weaker acids in table. A pH of 10 corresponds to a mildly basic solution—reasonable enough, for a weak base like OCl^- .

Not only can we use Eq. 14.7.4 to find the value of K_b for the base conjugate to a given acid, we can also employ it in the reverse sense to find the value of K_a for the acid conjugate to a given base, as the following example shows.

✓ Example 14.7.2: pH Calculation with K_b

Find the pH of 0.05 M NH_4Cl (ammonium chloride), using the value $K_b(\text{NH}_3) = 1.8 \times 10^{-5} \text{ mol L}^{-1}$.

Solution

We regard this solution as a solution of the weak acid NH_4^+ and start by finding K_a for this species:

$$K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{1.8 \times 10^{-5} \text{ mol L}^{-1}} \quad (14.7.18)$$

$$; = 5.56 \times 10^{-10} \text{ mol L}^{-1} \quad (14.7.19)$$

We can now evaluate the hydronium-ion concentration with the usual approximation:

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c_a} \quad (14.7.20)$$

$$= \sqrt{5.56 \times 10^{-10} \text{ mol L}^{-1} \times 0.05 \text{ mol L}^{-1}} \quad (14.7.21)$$

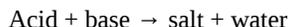
$$= 5.27 \times 10^{-6} \text{ mol L}^{-1} \quad (14.7.22)$$

whence pH = $-\log(5.27 \times 10^{-6}) = 5.28$

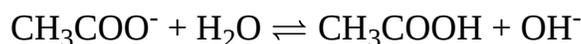
Note

The ammonium ion is a very weak acid (as seen in the [Tables of Ka and Kb values](#)). A solution of NH_4^+ ions will thus not produce a very acidic solution. A pH of 5 is about the same pH as that of black coffee, not very acidic.

Before the Brønsted-Lowry definition of acids and bases and the idea of conjugate acid-base pairs became generally accepted, the interpretation of acid-base behavior revolved very much around the equation



In consequence the idea prevailed that when an acid reacted with a base, the resultant salt should be neither acidic or basic, but neutral. In order to explain why a solution of sodium acetate was basic or a solution of ammonium chloride was acidic, a special term called **hydrolysis** had to be invoked. Thus, for instance, sodium acetate was said to be hydrolyzed because the acetate ion reacted with water according to the reaction



From the Brønsted-Lowry point of view there is, of course, nothing special about such a hydrolysis. It is a regular proton transfer. Nevertheless you should be aware of the existence of the term hydrolysis since it is still often used in this context.

Because the Brønsted-Lowry definition is so successful at explaining why some salt solutions are acidic and some basic, one must beware of making the mistake of assuming that no salt solutions are neutral. Many are. A good example is 0.10 M NaNO_3 . This solution is neutral because neither the Na^+ ion nor the NO_3^- ion shows any appreciable acidic or basic properties. Since NO_3^- is the conjugate base of HNO_3 we might expect it to produce a basic solution, but NO_3^- is such a weak base that it is almost impossible to detect such an effect. Just how weak a base NO_3^- is can be demonstrated using the value of $K_a(\text{HNO}_3) = 20 \text{ mol L}^{-1}$ obtained from the [Tables of Ka and Kb values](#).

$$K_b(\text{NO}_3^-); = \frac{K_w}{K_a(\text{HNO}_3)} \quad (14.7.23)$$

$$= \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{20 \text{ mol L}^{-1}} \quad (14.7.24)$$

$$= 5.0 \times 10^{-16} \text{ mol L}^{-1} \quad (14.7.25)$$

If we now apply the conventional formula [from equation 4 from the section on the pH of weak base solutions](#) to calculate $[\text{OH}^-]$ in 0.10 M NaNO_3 , we obtain

$$[\text{OH}^-] = \sqrt{K_b c_b} \quad (14.7.26)$$

$$= \sqrt{5.0 \times 10^{-16} \times 1.0 \times 10^{-1} \text{ mol L}^{-1}} \quad (14.7.27)$$

$$= 7.1 \times 10^{-9} \text{ mol L}^{-1} \quad (14.7.28)$$

But this is less than one-tenth the concentration of OH^- ion which would have been present in pure H_2O , with no added NaNO_3 . Essentially all the OH^- ions are produced by H_2O , and the pH turns out to be only slightly above 7.00. (Note also that the derivation of [equation 4 from the pH of weak base solutions section](#) assumed that the $[\text{OH}^-]$ produced by H_2O was negligible. To get an accurate result in this case requires a completely different equation.)

In general all salts in which group I and group II cations are combined with anions which are the conjugate bases of strong acids yield neutral solutions when dissolved in water. Examples are CaI_2 , LiNO_3 , KCl , $\text{Mg}(\text{ClO}_4)_2$.

There is only one exception to this rule. The hydrated beryllium ion, $\text{Be}(\text{H}_2\text{O})_4^{2+}$, is a weak acid ($K_a = 3.2 \times 10^{-7} \text{ mol L}^{-1}$) so that solutions of beryllium salts are acidic.

Table 14.7.1 The Acid-Base Properties of Some Common Ions

	Cations	Anions

Acidic	Cr ³⁺ , Fe ³⁺ , Al ³⁺ Hg ²⁺ , Be ²⁺ NH ₄ ⁺ , H ₃ O ⁺	HSO ₄ ⁻
Neutral	Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺ Li ⁺ , Na ⁺ , K ⁺ Ag ⁺	NO ₃ ⁻ , ClO ₄ ⁻ Cl ⁻ , Br ⁻ , I ⁻ SO ₄ ²⁻ (very weakly basic)
Basic	None	PO ₄ ³⁻ , CO ₃ ²⁻ , SO ₃ ²⁻ F ⁻ , CN ⁻ , OH ⁻ , S ²⁻ CH ₃ COO ⁻ , HCO ₃ ⁻

The table lists the acid-base properties of some of the more frequently encountered ions and provides a quick reference for deciding whether a given salt will be acidic, basic, or neutral in solution. Note that the table tells us nothing about the strength of any acid or base. If we need to know more about the pH, other than whether it is above, below, or equal to 7, we need information about the actual value of the acid or base constant. The table also lists the SO₄²⁻ ion as neutral, though classifying it as very feebly basic would be more accurate.

✓ Example 14.7.3: Acid, Base, or Neutral

Classify the following solutions as acidic, basic, or neutral: (a) 1 M KBr; (b) 1 M calcium acetate; (c) 1 M MgF₂; (d) 1 M Al(NO₃)₃; (e) 1 M KHSO₄; (f) 1 M NH₄I.

Solution

- Both cation and anion are neutral: neutral.
- Cation is neutral but anion basic: basic.
- Cation is neutral but anion basic: basic.
- Cation is acidic and anion neutral: acidic.
- Cation is neutral but anion acidic: acidic.
- Cation is acidic but anion neutral: acidic.

✓ Example 14.7.4: pH Matching

Without actually doing any calculations, match the following solutions and pH values, using the [Tables of Ka and Kb values](#), and the table on this page.

Aqueous Solution	pH
1 M NH ₄ NO ₃	8.0
1 M KCN	11.7
1 M Ca(NO ₃) ₂	9.4
1 M MgSO ₄	7.0
1 M CH ₃ COONa(sodium acetate)	1.0
1 M KHSO ₄	4.6

Solution

The pH of 7.0 is easiest to pick. Only one of the salt solutions given has both a neutral anion and a neutral cation. This is Ca(NO₃)₂. In the case of MgSO₄ the Mg²⁺ ion is neutral but the SO₄²⁻ ion is very feebly basic; this would agree with a pH of 8.0, only slightly basic. The SO₄²⁻ ion is such a feeble base because its conjugate acid, HSO₄⁻, is quite a strong acid, certainly the most acidic of all the ions featured. Accordingly we expect 1 M KHSO₄ to correspond to the lowest pH, namely, 1.0. The only other acidic solution is 4.6, and this must correspond to 1 M NH₄NO₃ since NO₃⁻ is the only other acidic ion present.

Among basic ions the cyanide ion, CN^- , is the strongest. The most basic pH, 11.7, thus corresponds to 1 M KCN. Only one solution is left: 1 M CH_3COONa . This should be feebly basic and so matches the remaining pH of 9.4 rather well.

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