

Deep Dive: Salt of Weak Acid AND Weak Base

(v 2.0)

1. PREAMBLE

The salts that usually appear in acid-base problems are one of these three types

Cation	Anion	Example
conjugate acid of a strong base (e.g., Na^+)	conjugate base of a strong acid (e.g., Cl^-)	NaCl
conjugate acid of a <i>weak</i> base (e.g., NH_4^+)	conjugate base of a strong acid (e.g., Cl^-)	NH_4Cl
conjugate acid of a strong base (e.g., Na^+)	conjugate base of a <i>weak</i> acid (e.g., CN^-)	NaCN

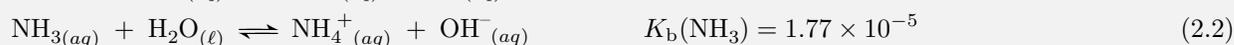
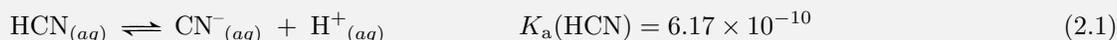
Each of the above salts has been covered previously. Notice at most either the cation or the anion are conjugates of something weak.

We now consider the very special case where both the cation and anion are conjugates of something weak. We will find (not surprisingly) that the solution's pH depends on the relative strengths of the cation and anion. Surprisingly, the numerical value of the pH will not depend on the concentration of the salt in the solution.

2. PROBLEM STATEMENT

Solid ammonia cyanide NH_4CN is dissolved in water. Find the resulting pH of the solution.

Data:



3. WHAT HAPPENS TO THE NH_4CN ?

Notice that no mention is made of the mass of salt added nor the volume of the solution. In other words, we do not know c the initial concentration of the salt. We will find the value of c will not matter.

When adding solid salt NH_4CN to liquid water this reaction happens



The value of K_{sp} , *solubility product constant*, for NH_4CN is so large that the reaction goes completely to the right. That is, all of the NH_4CN dissociates completely into NH_4^+ and CN^- . The *initial* molar concentrations of NH_4^+ and CN^- will equal the moles of solid NH_4CN added divided by the liters of solution. We define this ratio as c

$$[\text{NH}_4^+]_o = [\text{CN}^-]_o = c \quad \text{where} \quad c = \frac{\text{moles of solid } \text{NH}_4\text{CN added to water}}{\text{liters of solution}}$$

For the given problem statement there is no way for us to calculate c . It turns out its value is not needed.

4. WHAT HAPPENS TO NH_4^+ AND CN^- ?

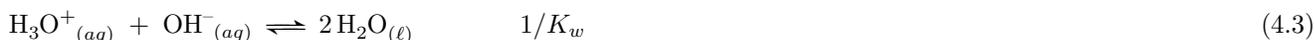
Since NH_4CN is completely soluble, the two ions NH_4^+ and CN^- will NOT reform NH_4CN . That is, the reverse of eq. (3.1) will not happen. However, each of ions will interact with water molecules (and there are a lot of water molecules around).

This two reactions below can occur (with appropriate equilibrium constants shown)

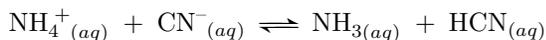


In previous problems at least one of the ions is from a strong acid or base and so previously we have been able to ignore one of the reactions above. However, here neither ion is from a strong acid or strong base. This means we are unable to ignore either of the above reactions. In other words, in this problem the salt will produce both H_3O^+ and OH^- . The resulting pH depends on the *relative* extent of both of the reactions (i.e., on $K_a(\text{NH}_4^+)$ vs $K_b(\text{CN}^-)$).

Things are further complicated by the fact that the H_3O^+ and OH^- ions can react with each other and form water via the autoionization reaction (with appropriate equilibrium constant shown)



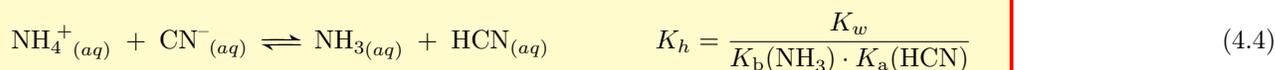
All three of the above reactions come into play in this problem. However, adding eqs. (4.1) to (4.3) we get the overall reaction



The reaction above has its own equilibrium constant. This will be the product of the equilibrium constants from eqs. (4.1) to (4.3)

$$K_h = [K_w/K_b(\text{NH}_3)] \cdot [K_w/K_a(\text{HCN})] \cdot [1/K_w] \quad \implies \quad K_h = \frac{K_w}{K_b(\text{NH}_3) \cdot K_a(\text{HCN})}$$

In conclusion, this is the net reaction between NH_4^+ and CN^- taking place in the water



This makes some sense. The weak acid and weak base produced by the solid salt do not reform the salt but instead exchange a proton to form a weak base and weak acid. The question, of course, is how successful is this exchange?

Important: Plugging in numbers we get quite a “large” value for K_h

$$K_h = \frac{1.00 \times 10^{-14}}{6.17 \times 10^{-10} \cdot 1.77 \times 10^{-5}} = 0.916$$

The other three equilibrium constants are much, much smaller than K_h .

$$K_w \ll K_h \quad \text{and} \quad K_a(\text{HCN}) \ll K_h \quad \text{and} \quad K_b(\text{NH}_3) \ll K_h$$

This means eq. (4.4) is the dominate equilibrium reaction.

5. WHAT IS THE FINAL EQUILIBRIUM OF EQ. (4.4)?

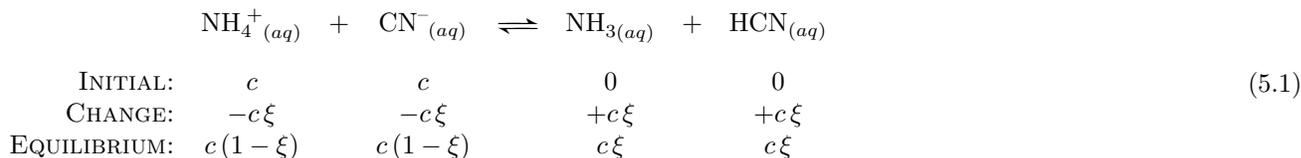
To get the final pH we need to get a grasp of the final equilibrium position of eq. (4.4).

It is convenient to define ξ the *extent of reaction* for eq. (4.4).

$$\xi = \frac{[\text{NH}_3]}{c} = \frac{[\text{HCN}]}{c} \quad \implies \quad 0 \leq \xi \leq 1$$

The above are the *equilibrium* concentrations. The extent of reaction expresses the final equilibrium as a number between 0 and 1. The value $\xi = 0$ means equilibrium is completely to the left. The value $\xi = 1$ means equilibrium is completely to the right.

Using ξ we can find expressions for the equilibrium concentrations for eq. (4.4)



Therefore, the equilibrium expression is

$$K_h = \frac{[\text{NH}_3] \cdot [\text{HCN}]}{[\text{NH}_4^+] \cdot [\text{CN}^-]} = \frac{c\xi \cdot c\xi}{c(1-\xi) \cdot c(1-\xi)} \quad \implies \quad K_h = \left(\frac{\xi}{1-\xi} \right)^2 \quad (\text{Note the } c\text{'s cancel!})$$

This can be solved for ξ . First, since $0 \leq \xi \leq 1$ the ratio $\xi/(1-\xi)$ can only be positive. This means when we take the square-root of both sides of the above we need only worry about the positive root

$$K_h = \left(\frac{\xi}{1-\xi} \right)^2 \quad \implies \quad \frac{\xi}{1-\xi} = \pm \sqrt{K_h} = \sqrt{K_h} \quad (\text{we can safely discard the negative root})$$

Therefore, we have this relationship between K_h and ξ (written in two ways)

$$\frac{\xi}{1-\xi} = \sqrt{K_h} \quad \text{or} \quad \xi = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}} \quad (5.2)$$

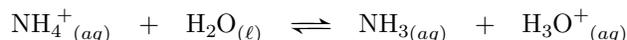
Important: If we plug in $K_h \approx 0.916$ from earlier, then we get

$$\xi = \frac{\sqrt{0.916}}{1 + \sqrt{0.916}} \approx 0.489$$

So without even knowing the concentration, at equilibrium the reaction eq. (4.4) appears to be balanced about half-way. That is, ξ is not close to zero and not close to one.

6. AN EXPRESSION FOR $[\text{H}_3\text{O}^+]$

To get an expression for the pH we can return to either eq. (4.1) or eq. (4.2). Why? We need a reaction that contains either H_3O^+ or OH^- . We will pick eq. (4.1) and use the equilibrium concentrations for NH_4^+ and NH_3 already found in eq. (5.1)



$$\text{EQUILIBRIUM:} \quad c(1-\xi) \qquad c\xi \qquad [\text{H}_3\text{O}^+]$$

The equilibrium expression for the above is

$$K_a(\text{NH}_4^+) = \frac{[\text{H}_3\text{O}^+] \cdot c\xi}{c(1-\xi)} = [\text{H}_3\text{O}^+] \frac{\xi}{1-\xi}$$

Notice that the c 's cancel again. Solving for the hydronium ion concentration we get

$$[\text{H}_3\text{O}^+] = \left(\frac{1-\xi}{\xi} \right) \cdot K_a(\text{NH}_4^+)$$

We can use our previous result from eq. (5.2) $\left(\frac{\xi}{1-\xi} \right) = \sqrt{K_h}$ to eliminate the ξ fraction. We get

$$[\text{H}_3\text{O}^+] = \left(\frac{1}{\sqrt{K_h}} \right) \cdot K_a(\text{NH}_4^+)$$

The above is what we want. Next, we put it in terms of the given equilibrium constants $K_a(\text{HCN})$ and $K_b(\text{NH}_3)$. Replace $K_a(\text{NH}_4^+)$ with $K_w/K_b(\text{NH}_3)$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{K_b(\text{NH}_3) \cdot \sqrt{K_h}}$$

Replace K_h with our previous result eq. (4.4) and simplify

$$[\text{H}_3\text{O}^+] = \frac{K_w}{K_b(\text{NH}_3) \cdot \sqrt{\frac{K_w}{K_b(\text{NH}_3) \cdot K_a(\text{HCN})}}} \quad \Rightarrow \quad [\text{H}_3\text{O}^+] = \sqrt{\frac{K_w \cdot K_a(\text{HCN})}{K_b(\text{NH}_3)}}$$

The above is now in terms of the given equilibrium constants. To find the pH we take the negative \log_{10} of both sides

$$-\log_{10}[\text{H}_3\text{O}^+] = \frac{1}{2} \left[-\log_{10} K_w \right] + \frac{1}{2} \left[-\log_{10} K_a(\text{HCN}) \right] - \frac{1}{2} \left[-\log_{10} K_b(\text{NH}_3) \right]$$

Or more simply

$$\text{pH} = 7 + \frac{\text{p}K_a(\text{HCN}) - \text{p}K_b(\text{NH}_3)}{2}$$

Notice two things about the above

- (i) The pH depends on the *relative* strengths of the conjugate acid and conjugate base making up the salt. That is, it depends on whether pK_a or pK_b is larger.
- (ii) The pH does NOT depend on c the concentration of the original solid salt.

Important: Plugging in numbers we have get

$$pK_a(\text{HCN}) = -\log_{10} K_a(\text{HCN}) = 9.209715\dots$$

$$pK_b(\text{NH}_3) = -\log_{10} K_b(\text{NH}_3) = 4.752027\dots$$

so

$$pH = 9.228844\dots \quad \implies \quad pH \approx 9.229$$

In the above, the original salt was NH_4CN where

- (i) NH_4^+ was the conjugate acid of the weak base NH_3
- (ii) CN^- was the conjugate base of the weak acid HCN

and we were provided with the K_a for HCN and K_b for NH_3 and the final pH was

$$pH = 7 + \frac{pK_a(\text{HCN}) - pK_b(\text{NH}_3)}{2}$$

We now generalize our result.

7. GENERALIZATION

Consider the solid salt BHA. This is an ionic compound whose unit formula could be written as BH^+A^- . The following dissociation reaction occurs when BHA is added to water

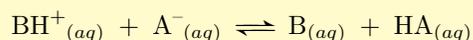


Thus, our salt BHA is made of two pieces

- (i) The cation BH^+ a conjugate acid of the weak base B
- (ii) The anion A^- a conjugate base of a weak acid HA

We will assume that we would be provided with the K_a for HA and K_b for B.

The dominate reaction in solution will be



The equilibrium constant and extent of reaction for the above will be

$$K_h = \frac{K_w}{K_b(\text{B}) \cdot K_a(\text{HA})} \quad \text{and} \quad \xi = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}$$

The final pH will be

$$pH = 7 + \frac{pK_a(\text{HA}) - pK_b(\text{B})}{2}$$

7.1. Final Note. We know that K_a for acetic acid CH_3COOH happens to equal the K_b for ammonia NH_3 . Since $pK_a = pK_b$, our formula implies that ammonium acetate $\text{NH}_4^+\text{CH}_3\text{COO}^-$ forms a solution with $pH = 7$. This is indeed the case.