Chem 116
Fall 2006
Prof. Sevian

Which of the following salts, when added to water, would produce the most acidic solution?
a) KBr b) NH_4NO_3 c) $AlCl_3$ d) Na_2HPO_4
(Assume the comparison is of equal molar quantities of each one added to water.)

Hydrolysis example problem similar to a text book exercise, Ex. 16.17, p. 701. From lecture notes 11-9-06.

Here is a comparison of what happens chemically and mathematically when each of these salts is added to water. Remember, a "salt" in the Bronsted-Lowry scheme is a conjugate of either an acid or a base, and sometimes both.

KBr

When KBr is added to water, it dissociates into K^+ and Br^-
$KBr\ (s) \rightarrow K^+\ (aq) + Br^-\ (aq)$

Does K^+ have a conjugate acid or base? No. It cannot accept an H^+ and it cannot donate an H^+.

Does Br^- have a conjugate acid or base? Yes, it can accept an H^+, so Br^- is a base and HBr is its conjugate acid.

What reaction could happen when Br^- reacts with water?
$Br^- + H_2O \leftrightarrows HBr + OH^-$
But this reaction does not occur to any reasonable extent because HBr is a strong acid, so the equilibrium in the reaction lies very strongly to the left.

Since no new H^+ or OH^- are produced, the resulting KBr (aq) solution remains as neutral as the original water solvent.

pH = 7

NH_4NO_3

When NH_4NO_3 is added to water, it dissociates into NH_4^+ and NO_3^-
$NH_4NO_3\ (s) \rightarrow NH_4^+\ (aq) + NO_3^-\ (aq)$

Does NH_4^+ have a conjugate acid or base? Yes. It can donate an H^+, so NH_4^+ is an acid and NH_3 is its conjugate base.

Does NO_3^- have a conjugate acid or base? Yes, it can accept an H^+, so NO_3^- is a base and HNO_3 is its conjugate acid.

What reaction could happen when NH_4^+ reacts with water?
$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$
This reaction occurs, since NH_4^+ is a weak acid and NH_3 is a weak base (*i.e.*, neither one is strong).

No reaction occurs between NO_3^- and water because HNO_3 is a strong acid (same argument as for Br^- at left).

Therefore, when NH_4NO_3 is added to water, the result is to increase the H_3O^+ concentration, so the solution becomes acidic.

pH < 7

$AlCl_3$

When $AlCl_3$ is added to water, it dissociates into Al^{3+} and Cl^-
$AlCl_3\ (s) \rightarrow Al^{3+}\ (aq) + 3\ Cl^-\ (aq)$
The aluminum ions form complexes with water. Al^{3+} ions don't exist in water, they become $[Al(H_2O)_6]^{3+}$ complex ions.

The aluminum complex ion can act like an acid and donate an H^+ to become $[Al(H_2O)_5(OH)]^{2+}$.

The Cl^- ion can accept an H^+, so Cl^- is a base and HCl is its conjugate acid. No reaction occurs between Cl^- and water because HCl is a strong acid (same argument as for Br^- at left).

The reaction that occurs between the aluminum complex ion and water is
$[Al(H_2O)_6]^{3+} + H_2O \leftrightarrows [Al(H_2O)_5(OH)]^{2+} + H_3O^+$
This reaction occurs since the complex on the reactant side is a weak acid, and the complex on the product side is a weak base (*i.e.*, neither one is strong).

Therefore, when $AlCl_3$ is added to water, the result is to increase the H_3O^+ concentration, so the solution becomes acidic.

pH < 7

Na_2HPO_4

When Na_2HPO_4 is added to water, it dissociates into Na^+ and HPO_4^{2-}
$Na_2HPO_4\ (s) \rightarrow 2\ Na^+\ (aq) + HPO_4^{2-}\ (aq)$

Does Na^+ have a conjugate acid or base? No. It cannot accept an H^+ and it cannot donate an H^+.

Does HPO_4^{2-} have a conjugate acid or base? Yes, it actually has both. It could accept an H^+, so HPO_4^{2-} is a base and $H_2PO_4^-$ is its conjugate acid. It could donate an H^+, so HPO_4^{2-} is also an acid and its conjugate base is PO_4^{3-}.

The reactions that could occur when HPO_4^{2-} is added to water are:
$HPO_4^{2-} + H_2O \leftrightarrows H_2PO_4^- + OH^-$
and
$HPO_4^{2-} + H_2O \leftrightarrows PO_4^{3-} + H_3O^+$

The first one is a K_b reaction, and from the table of K_a values, you can get K_b for HPO_4^{2-} acting as a base by $K_a K_b = K_w$. So, K_b for HPO_4^{2-} is 1.61×10^{-7}.

The second one is a K_a reaction, and from the table of K_a values, K_a for HPO_4^{2-} is 3.6×10^{-13}.

Comparing the two reactions, the first one produces much more than the second because the equilibrium constant for the first one is much larger than the equilibrium constant for the second. Therefore, when HPO_4^{2-} is added to water, the result is to increase the OH^- concentration, so the solution becomes basic.

pH > 7

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So, two of the choices produce acidic solutions: NH_4NO_3 and $AlCl_3$. The question now is, which one of them produces the most acidic solution. We want to know which of these reactions will produce more H_3O^+:

$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$ $K_a = 5.65\times10^{-10}$
or
$[Al(H_2O)_6]^{3+} + H_2O \leftrightarrows [Al(H_2O)_5(OH)]^{2+} + H_3O^+$ $K_a = 7.9\times10^{-6}$

So we just compare their K_a values. Whichever one has the larger K_a value must produce more H_3O^+. Therefore, the aluminum complex wins.

Answer: $AlCl_3$

Note: On an exam you wouldn't need to go to all this work, but I showed every single detail of the argument just to make everything clear. On an exam, the fastest way to solve this problem would be to split each ionic compound into its constituent ions. The + ion might be an acid if added to water. If so, it would produce some H_3O^+. The – ion might be a base if added to water. If so, it would produce some OH^-. In this question, since you're looking for the most acidic solution, you would just move forward with comparing the + ions that produce H_3O^+ to see which is a stronger acid.