

# 8

## H<sup>+</sup> Transfer Reactions: Relative Strengths of Acids

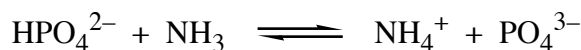
### Introduction

In this experiment, you will carry out some proton-transfer reactions. From your observations of each reaction, you will determine which of the two acids is stronger. You will draw conclusions not only by observing the reactions which take place, but also by observing the lack of reaction.

The proton-transfer reactions you will attempt are all of the type



for example,

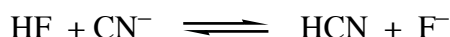


If you observe that a reaction occurs, you know that  $K$  is larger than 1 and  $\Delta G$  is negative. If the reaction does not happen appreciably, you know that  $K$  is less than 1 and  $\Delta G$  is positive.  $\Delta S$  is negligibly small for all of these reactions. (“2 pieces  $\rightarrow$  2 pieces”) The relative stability of the reactants and the products ( $\Delta G$ ) depends mostly on their bond strengths ( $\Delta H$ ). Looking at the simplified general reaction



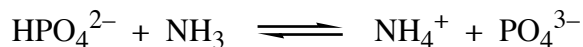
you can see that if the reaction goes, then the H–B bond is stronger than the H–A bond; the H<sup>+</sup> transfers so that it changes from weaker bonding to stronger bonding. If there is no reaction, that means the original H–A bond is stronger than the H–B bond could be, so the H<sup>+</sup> won’t transfer to the weaker bonding situation. Note that you get the same kind of information (which bond holding H is stronger) whether an attempted reaction goes or not!

If you tried to investigate the reaction



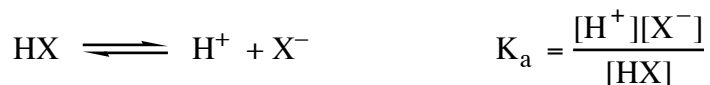
by mixing  $\text{CN}^-$  ions with aqueous HF, you would observe the formation of HCN (we will not do this reaction in the laboratory!!). Once you find that HF and  $\text{CN}^-$  will react, you know that the equilibrium lies to the right hand side of the reaction as written above. You also know that HCN and  $\text{F}^-$  will not react.

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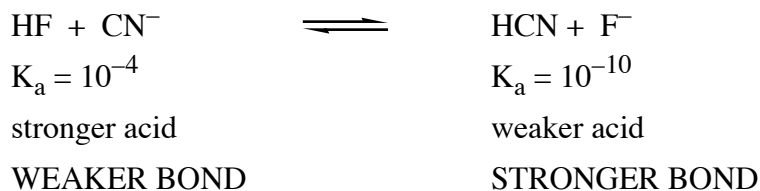
by mixing  $\text{HPO}_4^{2-}$  ions with aqueous  $\text{NH}_3$ , you would not observe any evidence of reaction. Once you find that  $\text{HPO}_4^{2-}$  and  $\text{NH}_3$  will not react, you know that the equilibrium lies to the left hand side of the reaction as written above. The reverse reaction behaves the opposite way, so you also know that  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  will react.

These aspects can be correlated with equilibrium-constant values ( $K_a$ ) for the two weak acids. The  $K_a$  for an acid, HX, refers to the simple ionization:

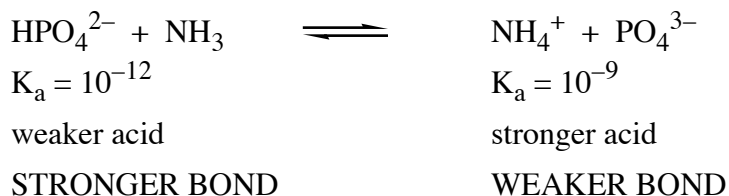


The stronger the bonding in the molecule HX, the lower the concentrations of the ions, thus the weaker the acid, and the lower the  $K_a$  value. Thus in a competition reaction, to decide whether the proton transfer will take place or not, you can compare the two  $K_a$  values to see which has a stronger bond (the weaker acid; the one with the smaller  $K_a$  value):

For example, here are the  $K_a$  values for the acids in the two previous examples:



The equilibrium lies to the RIGHT  $\rightarrow$ .



The equilibrium lies to the LEFT  $\leftarrow$ .

## Experimental Procedure

**SAFETY PRECAUTIONS:** Wear your SAFETY GOGGLES. If any of the acid solutions splashes on your skin or clothing, wash it off immediately with copious amounts of running water.

**WASTE DISPOSAL:** Pour all of the waste from this experiment down the drain, followed by plenty of running of water.

As you attempt each reaction described in this experimental section, record your observations in your notebook. You may find it very helpful to analyze the results of each reaction before proceeding to the next one.

- Put about 5 drops of 1 M HCl solution in each of two test tubes.
  - To one test tube, add some 0.1 M sodium benzoate (“NaBz”) solution. Record your observations. What is the precipitate? HCl is a strong acid; benzoic acid (“HBz”) is a weak acid and also has a low solubility in water.
  - To the other test tube of HCl solution, add some 1 M NaHCO<sub>3</sub>. Record your observations. Can you explain the results?
- Put about 5 drops of 1 M NaHSO<sub>4</sub> solution in each of two test tubes.
  - To one tube, add some 0.1 M sodium benzoate. Record your observations.
  - To the other tube, add some 1 M NaHCO<sub>3</sub>. Record your observations.
- Put about 5 drops of 1 M acetic acid (“HAc”) in each of two test tubes.
  - To one test tube, add some 1 M NaHCO<sub>3</sub>. Record your observations.
  - To the other tube, add some 0.1 M sodium benzoate solution. Record your observations.
- Confirm your results for reaction (3b) above by trying to dissolve a small sample of solid benzoic acid in some 1 M sodium acetate solution. The sample of benzoic acid should be as small as possible but “big enough to see”! Record the number of drops of sodium acetate solution needed to dissolve it. Record your observations.

To be sure that the acetate ion is actually helping to dissolve the benzoic acid, for comparison try to dissolve a similar sized sample of the solid benzoic acid in the same volume of plain water. The volume of water should be the same as the volume of sodium acetate solution used -- the same number of drops. Record your observations.

Do your results for reaction (4) agree with your results for reaction (3b)? Explain.

- Plan two different experiments to determine the relative strengths of the two acids: bisulfite ion (HSO<sub>3</sub><sup>-</sup>) or benzoic acid (HBz). (Which is the stronger acid and which is the weaker acid?) Important: you cannot just combine the two substances (NaHSO<sub>3</sub> and HBz), because then one of them would be acting as an acid and the other would be acting as a base. Look at the patterns in the previous reactions to help

you determine which compounds to mix. Write the net ionic equations, then perform the reactions and record your observations.

### Analysis

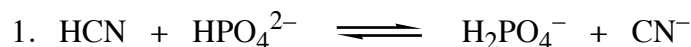
For each of the  $H^+$  transfer reactions attempted in this experiment, answer the following questions, based on your experimental observations:

- Write the net ionic equation for the reaction that you attempted. (Be sure to leave out ions that are not involved, such as  $Na^+$ ,  $K^+$ , etc. Remember that strong acids should be written as separate ions, since they are mostly in that form. Weak acids should be written as molecules, since they are mostly in that form.)
- Do your observations indicate that the equilibrium lies to the left or to the right?
- Which is the stronger acid? Which is the weaker acid?
- Which acid has the stronger bond holding  $H^+$ ?

Finally, compare your experimental results with accepted  $K_a$  values. Go back to the net ionic equations for the reactions that you attempted in the laboratory. Look up the  $K_a$  values in your textbook for all of the weak acids. Write the  $K_a$  values under the formula of the weak acid wherever it appears in an equation. Check to confirm that the lower  $K_a$  value indicates the stronger bond in each case.

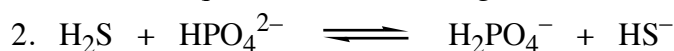
### Pre-Lab Questions:

For the following reactions, look up  $K_a$  values in your textbook to help answer the questions. None of these reactions will be done in the lab.



Label each of the above species as an acid or a base. For each of the acids, write the  $K_a$  value below its formula.

Will the above reaction take place spontaneously? (Is the reaction product-favored? Does the equilibrium lie to the right?)



Label each of the above species as an acid or a base. For each of the acids, write the  $K_a$  value below its formula.

Will the above reaction take place spontaneously? (Is the reaction product-favored? Does the equilibrium lie to the right?)

- If you mix  $NaHCO_3$  with  $K_3PO_4$ , what is the net ionic equation for the (potential)  $H^+$  transfer? Will it take place spontaneously?
- If you mix  $K_2HPO_4$  with  $NaAc$  (sodium acetate), what is the net ionic equation for the (potential)  $H^+$  transfer? Will it take place spontaneously?