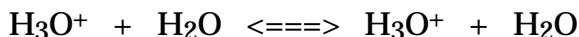


## Part I: The pK<sub>a</sub> of H<sub>3</sub>O<sup>+</sup> and H<sub>2</sub>O

### 1) What is the pK<sub>a</sub> of H<sub>3</sub>O<sup>+</sup>?



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+][\text{H}_2\text{O}]}$$

Multiplying both sides by [H<sub>2</sub>O] will give:

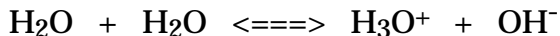
$$K_c [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]}$$

Noting that  $K_c [\text{H}_2\text{O}] = K_a$  and  $[\text{H}_3\text{O}^+]$  cancels out, we arrive at:

$$K_a = [\text{H}_2\text{O}] = 55.5 \text{ M}$$

$$\text{pK}_a = -\log 55.5 = -\log 10^{1.74} = -1.74$$

### 2) What is the pK<sub>a</sub> of H<sub>2</sub>O?



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

Multiplying both sides by [H<sub>2</sub>O] will give:

$$K_c [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Noting that  $K_c [\text{H}_2\text{O}] = K_a$  and  $[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$ , we arrive at:

$$K_a = \frac{K_w}{[\text{H}_2\text{O}]}$$

$$K_a = (1.00 \times 10^{-14} \div 55.5) = (10^{-14} \div 10^{1.74}) = 10^{-15.74}$$

$$\text{pK}_a = -\log 10^{-15.74} = 15.74$$

### 3) How do $\text{H}_3\text{O}^+$ and $\text{H}_2\text{O}$ compare to each other in terms of acidic strength?

$$\Delta\text{pK}_a = 15.74 - (-1.74) = 17.48$$

Conclusion:  $\text{H}_3\text{O}^+$  is a stronger acid than  $\text{H}_2\text{O}$  is by a factor of  $10^{17.48}$ .

### 4) How do other acids and bases compare to these two?

a) An acid (such as HCl) with a  $\text{pK}_a$  less than  $-1.74$  is always fully ionized in  $\text{H}_2\text{O}$ . These acids all level out to the  $\text{pK}_a$  of  $\text{H}_3\text{O}^+$ .

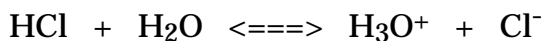
b) Between the limits of  $\text{pK}_a = -1.74$  ( $\text{H}_3\text{O}^+$ ) and  $15.74$  ( $\text{H}_2\text{O}$ ), the extent of ionization is directly proportional to the  $\Delta\text{pK}_a$ .

## Part II: The Extent of Acid Base Reactions

Nature always favors the weaker acid/base pair.

Remember the definition of  $\text{pK}_a$ :  $-\log K_a$ . The lower the  $\text{pK}_a$ , the stronger the acid.

### Example #1

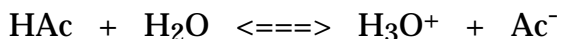


The  $\text{pK}_a$  of HCl =  $-7$ . The  $\text{pK}_a$  of  $\text{H}_3\text{O}^+$  =  $-1.74$ .

$$\Delta\text{pK}_a = -7 - (-1.74) = -5.26$$

This is an decrease in acid strength (from HCl to  $\text{H}_3\text{O}^+$ ) by a factor of  $1.82 \times 10^5$ . This reaction is running downhill thermodynamically. Result: HCl is fully ionized in water solution. It is a strong acid.

### Example #2

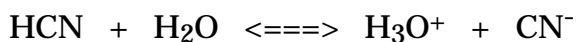


The  $\text{pK}_a$  of HAc =  $4.75$ . The  $\text{pK}_a$  of  $\text{H}_3\text{O}^+$  =  $-1.74$ .

$$\Delta\text{pK}_a = 4.75 - (-1.74) = 6.49$$

This is an increase in acid strength (from HAc to  $\text{H}_3\text{O}^+$ ) by a factor  $3.24 \times 10^7$ . This reaction is running uphill thermodynamically. Result: acetic acid is partially ionized in water solution. It is a weak acid.

### Example #3



The  $\text{pK}_a$  of HCN = 11. The  $\text{pK}_a$  of  $\text{H}_3\text{O}^+$  = -1.74.

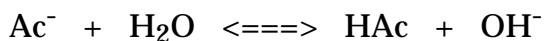
$$\Delta\text{pK}_a = 11 - (-1.74) = 12.74$$

This is an increase of acid strength (from HCN to  $\text{H}_3\text{O}^+$ ) by a factor  $5.50 \times 10^{12}$ . This reaction is running uphill thermodynamically. Result: HCN is partially ionized in water solution. It is a weak acid.

Question: which is ionized more - 0.1 M HAc or 0.1 M HCN?

Answer: The HAc since it has less of an uphill battle to ionize than the HCN does.

### Example #4

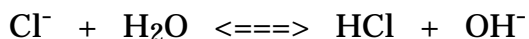


The  $\text{pK}_a$  of  $\text{H}_2\text{O}$  is 15.74. The  $\text{pK}_a$  of HAc is 4.75.

$$\Delta\text{pK}_a = 15.74 - 4.75 = 10.99$$

This is an increase of acid strength (from  $\text{Ac}^-$  to HAc) by a factor  $9.77 \times 10^{10}$ . This reaction is running uphill thermodynamically. Result:  $\text{Ac}^-$  partially hydrolyzes in water. It forms a slightly basic solution.

### Example #5

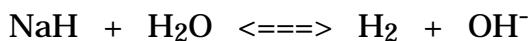


The  $\text{pK}_a$  of  $\text{H}_2\text{O}$  is 15.74. The  $\text{pK}_a$  of HCl is -7.

$$\Delta\text{pK}_a = 15.74 - (-7) = 22.74$$

This is an increase of acid strength (from  $\text{H}_2\text{O}$  to HCl) by a factor  $5.50 \times 10^{22}$ . This reaction is running uphill thermodynamically. Result:  $\text{Cl}^-$  does not hydrolyze in water. It forms a neutral solution.

### Example #6



The  $\text{pK}_a$  of  $\text{H}_2\text{O}$  is 15.74. The  $\text{pK}_a$  of  $\text{H}_2$  is 33.

$$\Delta\text{pK}_a = 15.74 - 33 = -17.26.$$

This is a decrease of acid strength (from  $\text{H}_2\text{O}$  to  $\text{H}_2$ ) by a factor  $1.82 \times 10^{17}$ . This reaction is running downhill thermodynamically. Result: NaH reacts strongly with water, the  $\text{H}_2$  escapes, leaving a basic solution.