

ACIDS & BASES

BRØNSTED ACIDS & BASES

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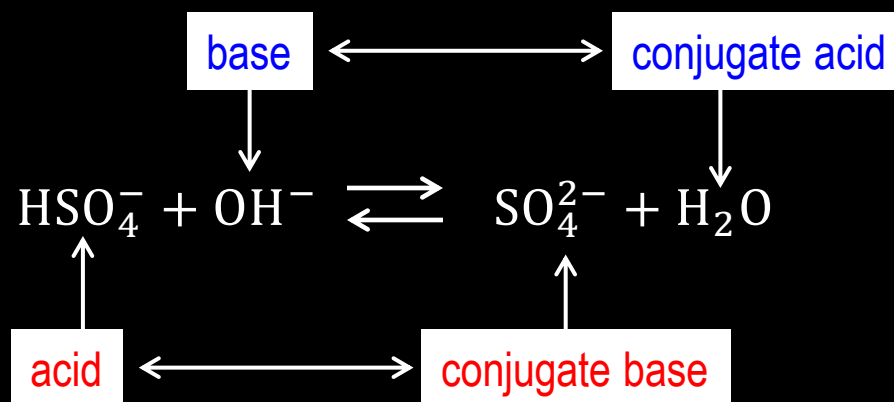
Brønsted acids are proton donors.

Brønsted bases are proton acceptors.

Amphoteric species can act as either an acid or a base, depending on the conditions.



CONJUGATE ACIDS/BASES: CONJUGATE PAIRS



STRENGTHS OF ACIDS

MOLECULAR STRUCTURE AND STRENGTH

What determines the strength of an acid is how easy it is to remove the acidic proton.

There are two things to consider:

1.) How easy it is to break the bond between the acidic proton and the rest of the molecule.

a.) Bond length (longer = easier to break)

b.) Polarity (more polar = easier to break)

2.) How stable the conjugate base of the acid is after removing the acidic proton.

a.) For a monatomic anion, more E.N. = more stable

b.) For a polyatomic anion, delocalization of charge = more stable

THE HYDROHALIC ACIDS

Relative acidity:



Even though the fluoride ion is the most stable (F is most E.N.), the length of the H-X bond is more important here.

THE OXOACIDS

An acid that has one or more oxygen atoms along with another element.

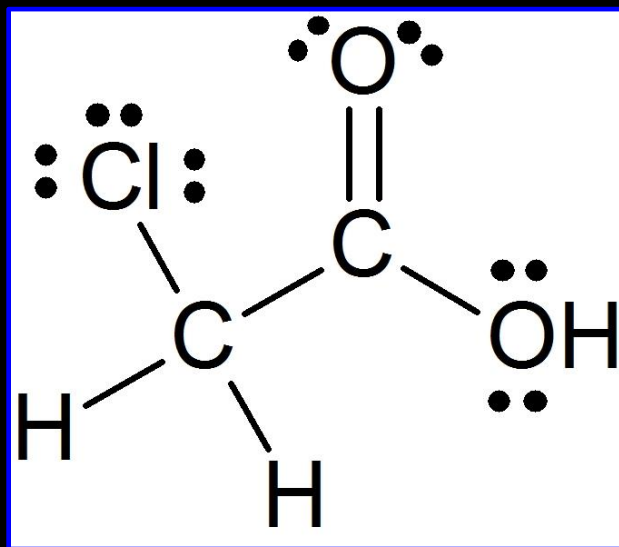
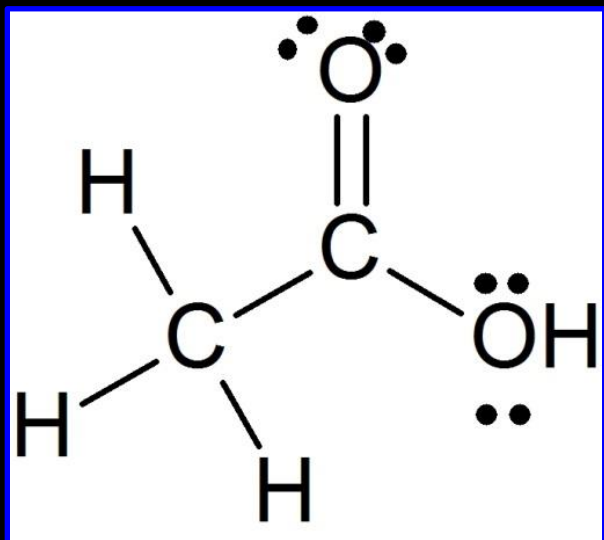
Nitric acid, nitrous acid, sulfuric acid, sulfurous acid, perchloric acid, hypoiodous acid etc.

Same central atom, different number of oxygen atoms: More oxygen atoms mean the anion has more resonance forms and is more stable, making the acid stronger.

Different central atom, same number of oxygen atoms: the more E.N. central atom makes the bond more polar, and also stabilizes the resulting anion more making the acid stronger.

CARBOXYLIC ACIDS

Organic acids of the form RCO_2H where "R" is the general symbol for a group containing C and/or H, and maybe other elements.



ACID-BASE PROPERTIES OF WATER

THE AUTOIONIZATION OF WATER



or



$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-]$$

or

$$K_W = [\text{H}^+][\text{OH}^-]$$

At 25°C in pure water $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$

or

$$K_W = 1.0 \times 10^{-14}$$

AQUEOUS SOLUTIONS

In any aqueous solution, not just pure water:

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

If $[\text{H}^+] = [\text{OH}^-]$ then the solution is neutral

If $[\text{H}^+] > [\text{OH}^-]$ then the solution is acidic

If $[\text{H}^+] < [\text{OH}^-]$ then the solution is basic

pH

THE pH SCALE

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$\text{pH} + \text{pOH} = 14$$

$[\text{H}_3\text{O}^+] (M)$	$-\log [\text{H}_3\text{O}^+]$	pH		
0.10	$-\log (1.0 \times 10^{-1})$	1.00	↑	
0.010	$-\log (1.0 \times 10^{-2})$	2.00		
1.0×10^{-3}	$-\log (1.0 \times 10^{-3})$	3.00		
1.0×10^{-4}	$-\log (1.0 \times 10^{-4})$	4.00		
1.0×10^{-5}	$-\log (1.0 \times 10^{-5})$	5.00		
1.0×10^{-6}	$-\log (1.0 \times 10^{-6})$	6.00		Acidic
1.0×10^{-7}	$-\log (1.0 \times 10^{-7})$	7.00		Neutral
1.0×10^{-8}	$-\log (1.0 \times 10^{-8})$	8.00	Basic	
1.0×10^{-9}	$-\log (1.0 \times 10^{-9})$	9.00	↓	
1.0×10^{-10}	$-\log (1.0 \times 10^{-10})$	10.00		
1.0×10^{-11}	$-\log (1.0 \times 10^{-11})$	11.00		
1.0×10^{-12}	$-\log (1.0 \times 10^{-12})$	12.00		
1.0×10^{-13}	$-\log (1.0 \times 10^{-13})$	13.00		
1.0×10^{-14}	$-\log (1.0 \times 10^{-14})$	14.00		

$[\text{OH}^-] (M)$	pOH		
0.10	1.00	↑	
1.0×10^{-3}	3.00		
1.0×10^{-5}	5.00		Basic
1.0×10^{-7}	7.00		Neutral
1.0×10^{-9}	9.00		Acidic
1.0×10^{-11}	11.00		↓
1.0×10^{-13}	13.00		

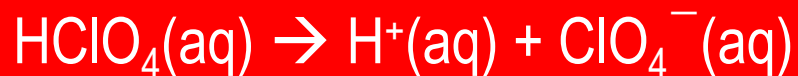
STRONG ACIDS & STRONG BASES

THE STRONG ACIDS

- Hydrochloric acid
- Hydrobromic acid
- Hydroiodic acid
- Nitric acid
- Chloric acid
- Perchloric acid
- Sulfuric acid (only the first acidic proton completely dissociates)

These acids completely dissociate in water

The $[\text{H}_3\text{O}^+] = [\text{acid}]$ because they completely dissociate.



THE STRONG BASES

- Lithium hydroxide
- Sodium hydroxide
- Potassium hydroxide
- Rubidium hydroxide
- Cesium hydroxide
- Calcium hydroxide
- Strontium hydroxide
- Barium hydroxide

These bases completely dissociate in water

The $[\text{OH}^-] = [\text{base}]$ (or $2x[\text{base}]$) because they completely dissociate.

Even though calcium hydroxide and strontium hydroxide are only slightly soluble, what does dissolve does so completely.



WEAK ACIDS AND K_a

$$K_a$$

If an acid is not a strong acid, it is a weak acid.

Weak acids do not completely dissociate in water, but rather exist at equilibrium:

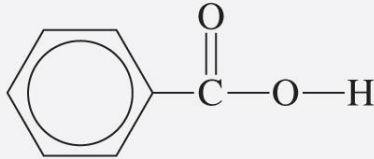
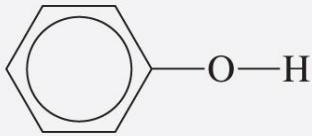


The equilibrium expression is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

K_a is the acid ionization constant

K_a

Name of acid	Formula	Structure	K_a
Chloroacetic acid	CH_2ClCOOH	$\text{CH}_2\text{Cl}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$	5.6×10^{-2}
Hydrofluoric acid	HF	H—F	7.1×10^{-4}
Nitrous acid	HNO_2	$\text{O}=\text{N}-\text{O}-\text{H}$	4.5×10^{-4}
Formic acid	HCOOH	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$	1.7×10^{-4}
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$		6.5×10^{-5}
Acetic acid	CH_3COOH	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$	1.8×10^{-5}
Hydrocyanic acid	HCN	$\text{H}-\text{C}\equiv\text{N}$	4.9×10^{-10}
Phenol	$\text{C}_6\text{H}_5\text{OH}$		1.3×10^{-10}

CALCULATING pH FROM K_a

Calculating pH means finding $[H^+]$. This is an equilibrium problem, so we set up an i.c.e. table.

Example:

Calculate the pH of a solution whose initial concentration of acetic acid is 0.454 M.

$$\text{pH} = 2.54$$

PERCENT IONIZATION

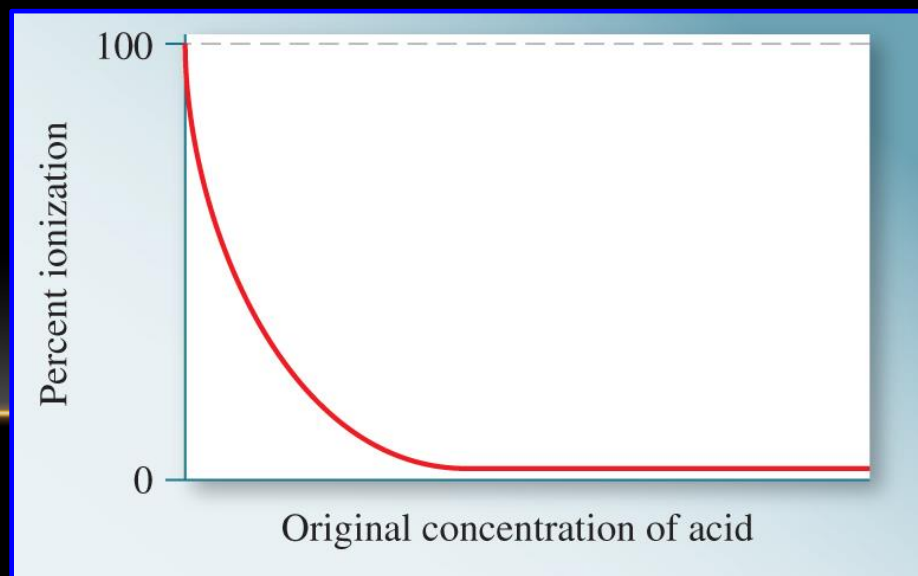
$$\% \text{ ionization} = \frac{[\text{H}^+]_{eq}}{[\text{HA}]_0} \times 100$$

In general if the % ionization is $< 5\%$ we can assume that

$[\text{H}^+]_{eq} \ll [\text{HA}]_0$ and can be neglected in the denominator of the equilibrium expression.

Otherwise the quadratic formula must be used.

% ionization increases as the $[\text{HA}]_0$ approaches zero.



PERCENT IONIZATION

What is the percent ionization of acetic acid in the preceding example?

$$= \frac{2.8_{49} \times 10^{-3}}{0.454} \times 100 = 0.62_7\%$$

Therefore it was safe to neglect $[\text{H}^+]_{\text{eq}}$ in the equilibrium expression.

WEAK BASES AND K_b

$$K_b$$

If an base is not a strong base, it is a weak base.

Weak bases do not completely dissociate in water, but rather exist at equilibrium:

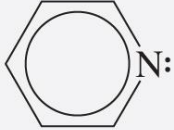
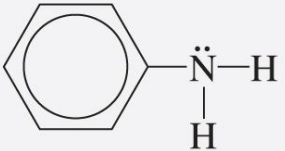


The equilibrium expression is

$$K_a = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

K_b is the base ionization constant

K_b

Name of base	Formula	Structure	K_b
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\overset{\cdot\cdot}{N}-H$ H	5.6×10^{-4}
Methylamine	CH_3NH_2	$CH_3-\overset{\cdot\cdot}{N}-H$ H	4.4×10^{-4}
Ammonia	NH_3	$H-\overset{\cdot\cdot}{N}-H$ H	1.8×10^{-5}
Pyridine	C_5H_5N		1.7×10^{-9}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}
Urea	H_2NCONH_2	$H-\overset{\cdot\cdot}{N}-\overset{O}{\parallel}C-\overset{\cdot\cdot}{N}-H$ H H	1.5×10^{-14}

CALCULATING pH FROM K_b

Calculating pH means finding $[H^+]$. This is an equilibrium problem, so we set up an i.c.e. table.

Example:

Calculate the pH of a solution whose initial concentration of ethylamine is 0.0519 M.

$$\text{pH} = 11.71$$

(% ionization = 9.9%, so had to use the quadratic formula)

K_a FROM pH

What is the value of K_a for a weak acid if a 0.519 M solution of the acid gives a solution with pH = 2.34?

$$K_a = 4.1 \times 10^{-5}$$

K_b FROM pH

What is the value of K_b for a weak base if a 0.398 M solution of the base gives a pH of 9.44?

$$K_b = 1.9 \times 10^{-9}$$

CONJUGATE ACID-BASE PAIRS

CONJUGATE'S STRENGTHS

The conjugate base of a strong acid is a weak conjugate base.

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The conjugate base of a weak acid is a strong conjugate base*

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* A strong conjugate base is a weak base

* A strong conjugate acid is a weak acid.

Acid	Example	Conjugate base	Formula	Base	Example	Conjugate acid	Formula
strong	HNO ₃	weak conjugate	NO ₃ ⁻	strong	OH ⁻	weak conjugate	H ₂ O
weak	HCN	strong conjugate	CN ⁻	weak	NH ₃	strong conjugate	NH ₄ ⁺

K_b , K_a , and K_w

$$K_b \times K_a = K_w$$

$$pK_b + pK_a = 14$$

The K_a for nitrous acid is 4.5×10^{-4} . What is K_b for the nitrite ion?

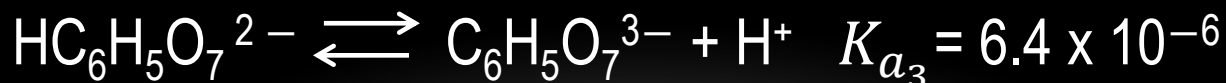
$$K_b = 2.2 \times 10^{-11}$$

POLYPROTIC ACIDS

POLYPROTIC ACIDS

Acids that have more than one acidic proton lose them successively. The K_a 's are labeled K_{a_1} , K_{a_2} , and K_{a_3} (if there is a third acidic proton).

$$K_{a_1} > K_{a_2} > K_{a_3}$$



Acid Name		K_a	pK_a
Carbonic, H_2CO_3	1 st	4.5×10^{-7}	6.35
	2 nd	4.7×10^{-11}	10.33
Hydrogen sulphide, H_2S	1 st	9.5×10^{-8}	7.02
	2 nd	1.0×10^{-19}	19.0
Phosphoric acid, H_3PO_4	1 st	7.1×10^{-3}	2.15
	2 nd	6.3×10^{-8}	7.20
	3 rd	4.5×10^{-13}	12.35
Sulphuric acid, H_2SO_4	1 st	large	
	2 nd	1.2×10^{-2}	1.92
Telluric acid, H_6TeO_6	1 st	2.0×10^{-8}	7.7
	2 nd	1.0×10^{-11}	11.0
	3 rd	3.0×10^{-15}	14.5
Sulphurous acid, H_2SO_3	1 st	1.2×10^{-2}	1.92
	2 nd	6.6×10^{-8}	7.18
Selenous acid, H_2SeO_3	1 st	3.5×10^{-3}	2.46
	2 nd	5.0×10^{-8}	7.3
Tellurous acid, H_2TeO_3	1 st	3.0×10^{-3}	2.5
	2 nd	2.0×10^{-8}	7.7
Ascorbic acid, $H_2C_6H_6O_6$	1 st	7.9×10^{-5}	4.10
	2 nd	1.6×10^{-12}	11.79
Citric acid, $H_3C_6H_5O_7$	1 st	7.1×10^{-4}	3.15
	2 nd	1.7×10^{-5}	4.77
	3 rd	6.4×10^{-6}	5.19

Calculate the concentrations of all species present at equilibrium in a 0.25 M solution of citric acid at 25°C.

$$[\text{H}_3\text{C}_6\text{H}_5\text{O}_7] = 0.24 \text{ M}$$

$$[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-] = 0.013 \text{ M}$$

$$[\text{HC}_6\text{H}_5\text{O}_7^{2-}] = 0.000017 \text{ M}$$

$$[\text{C}_6\text{H}_5\text{O}_7^{3-}] = 0.0000000084 \text{ M}$$

$$[\text{H}^+] = 0.013 \text{ M}$$

SALTS AS ACIDS AND BASES

SALT HYDROLYSIS

When a strong electrolyte is dissolved in water, if the anion is the conjugate base of a weak acid, or the cation is the conjugate acid of a weak base, hydrolysis occurs affecting the pH of the solution. For example, if a 0.150 M solution of KF is prepared, the following occurs:

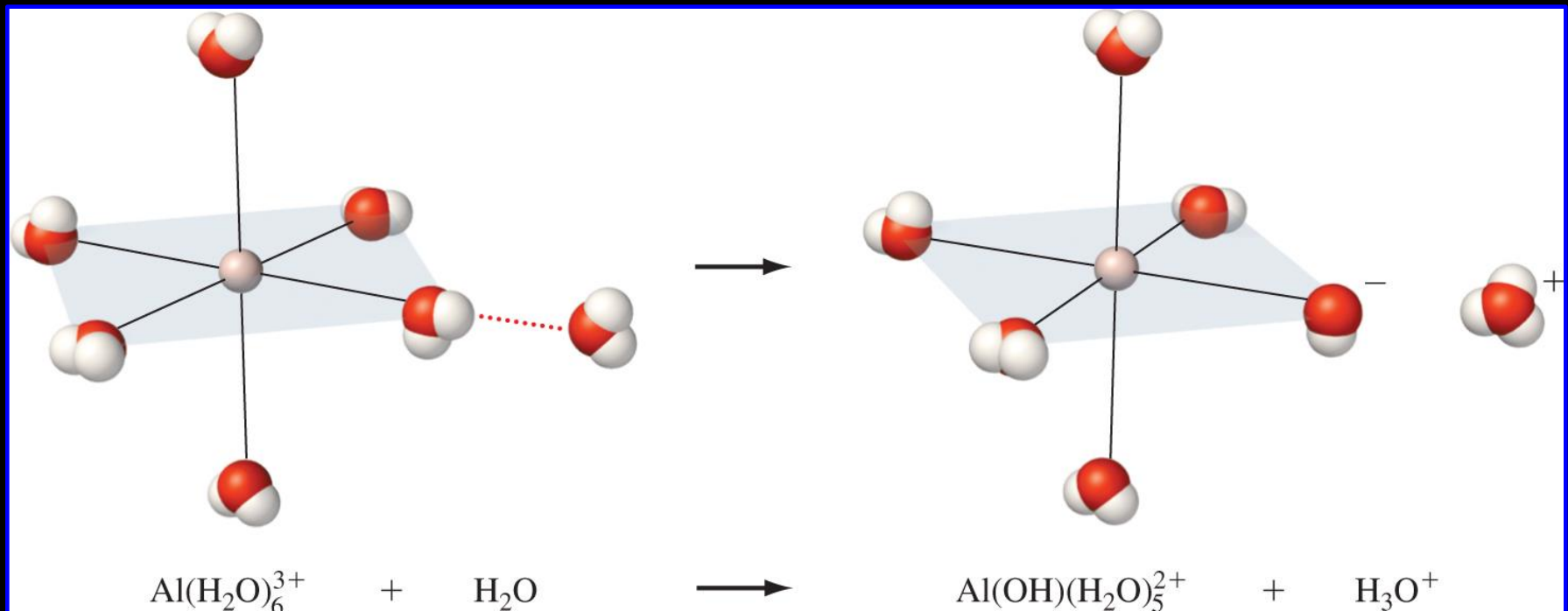
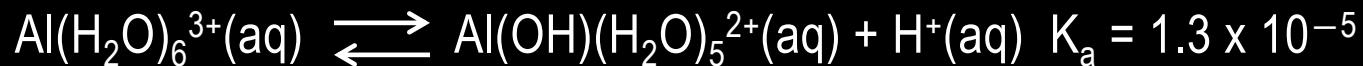


What is the pH of the resulting solution? K_a for HF = 7.1×10^{-4}

$$\text{pH} = 8.18$$

THE METAL CATION CAN ALSO REACT WITH H₂O

Small, highly charged metal cations such as Al³⁺, Cr³⁺, Fe³⁺, Bi³⁺, and Be²⁺ associate with water molecules through ion-dipole interactions. For example the aluminum ion:



SALT SOLUTIONS

Metal cations that are relatively large and/or not highly charged do not undergo hydrolysis. Thus, the group 1A and 2A metals (except Be) do not do this.

Anions that are conjugate bases of strong acids do not undergo hydrolysis either.

If both the cation and anion hydrolyze:

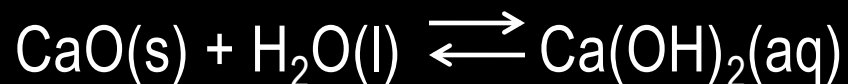
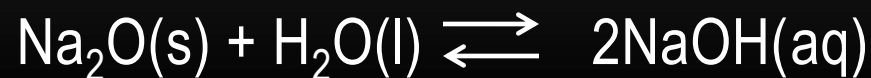
If $K_a > K_b$ the solution is acidic

If $K_b > K_a$ the solution is basic

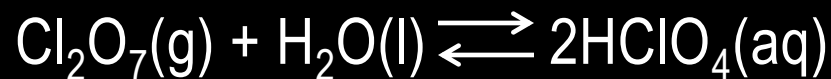
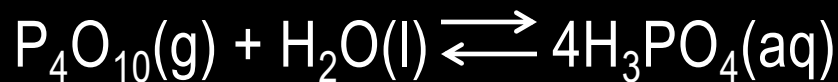
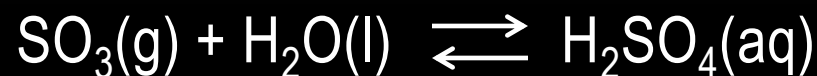
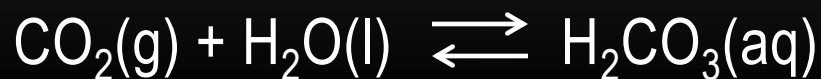
If $K_a \approx K_b$ the solution is neutral, or close to neutral.

OXIDES AND HYDROXIDES

ALKALI METAL OXIDES AND ALKALINE EARTH METAL HYDROXIDES ARE BASIC (EXCEPT BeO WHICH IS AMPHOTERIC)



NONMETAL OXIDES WHOSE NONMETAL HAS A HIGH OXIDATION NUMBER ARE ACIDIC



LEWIS ACIDS AND BASES

DEFINITIONS

A Lewis acid is an electron pair donor.

A Lewis base is an electron pair acceptor.

In every Lewis-base reaction a coordinate covalent bond is formed.

