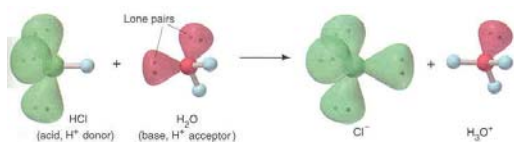


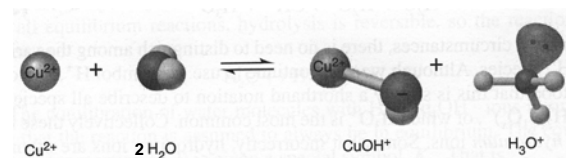
Acidic and Basic Solutes

- Acids always increase the concentration of H_3O^+ and decrease that of OH^- .
- Some acids release H^+ ions directly when they dissociate:

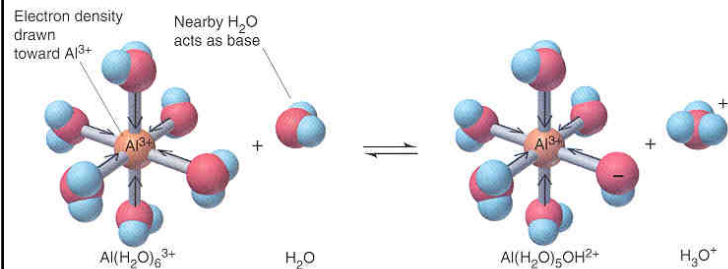


Acidic and Basic Solutes

- Other acids increase H^+ concentration by causing a water molecule to split (**hydrolyze**) and combining with the OH^- (in that order or the reverse):

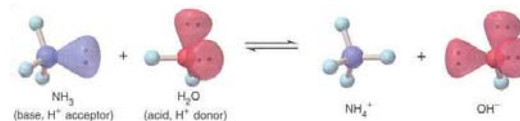
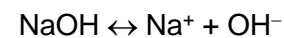


Acidic and Basic Solutes



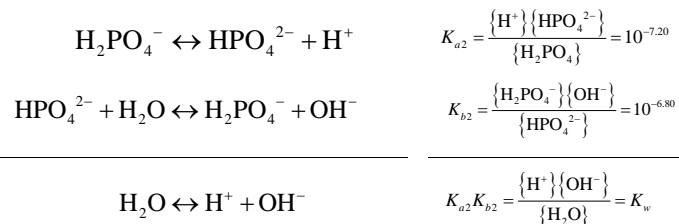
Acidic and Basic Solutes

- Bases always decrease the concentration of H_3O^+ and increase that of OH^- .
- Some bases release OH^- ions directly when they dissociate, while others extract an H^+ from a water molecule:



Acid/Base Chemistry

- The summation of an acid dissociation reaction and the basicity reaction for the conjugate base always yields the dissociation reaction of water:



Acid/Base Chemistry

- Since all K_a 's have the following form, K_a is a direct indicator of the tendency to donate an H^+ ; i.e., the **strength** of the acid.



$$K_a = \frac{\{\text{Conjugate Base}\}\{\text{H}^+\}}{\{\text{Acid}\}}$$

In a given solution (given $\{\text{H}^+\}$) containing several acid/base pairs, larger K_a corresponds to greater acid dissociation.

Acid/Base Chemistry

- Since $\text{p}K_a$ increases when K_a decreases, stronger acids have **lower** $\text{p}K_a$ values.
- Since K_aK_b equals K_w , the larger K_a , the smaller K_b for the conjugate base, and vice versa. Therefore, strong acids have weak conjugate bases, and weak acids have strong conjugate bases. Put another way, if the acid is likely to dissociate, the base is unlikely to re-associate.

Name	Formula	$\text{p}K_{a1}$	$\text{p}K_{a2}$	$\text{p}K_{a3}$
Nitric acid	HNO_3	-1.30		
Trichloroacetic acid	CCl_3COOH	-0.5		
Hydrochloric acid	HCl	<0		
Sulfuric acid	H_2SO_4	<0	1.99	
Hydronium ion	H_3O^+	0.00	14.00	
Chromic acid	H_2CrO_4	0.86	6.51	
Oxalic acid	$(\text{COOH})_2$	0.90	4.20	
Dichloroacetic acid	CHCl_2COOH	1.1		
Sulfurous acid	H_2SO_3	1.86	7.30	
Phosphoric acid	H_3PO_4	2.16	7.20	12.35
Arsenic acid	H_3AsO_4	2.24	6.76	11.60
Monochloroacetic acid	CH_2ClCOOH	2.86		
Salicylic acid	$\text{C}_6\text{H}_4\text{OHCOOH}$	2.97	13.70	
Citric acid	$\text{C}_3\text{H}_5\text{OH}(\text{COOH})_3$	3.13	4.72	6.33
Hydrofluoric acid	HF	3.17		
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	4.20		
Pentachlorophenol	$\text{C}_6\text{Cl}_5\text{OH}$	4.7		
Acetic acid	CH_3COOH	4.76		
Carbonic acid	H_2CO_3	6.35	10.33	

Name	Formula	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}
Hydrogen sulfide	H ₂ S	6.99	12.92		
Hypochlorous acid	HOCl	7.60			
Cupric ion	Cu ²⁺	8.00	5.68		
2-Chloro-phenol	C ₆ H ₄ ClOH	8.53			
Hypobromous acid	HOBr	8.63			
Zinc ion	Zn ²⁺	8.96	8.94		
Arsenous acid	H ₃ AsO ₃	9.23	12.10		
Hydrocyanic acid	HCN	9.24			
Boric acid	H ₃ BO ₃	9.24			
Ammonium ion	NH ₄ ⁺	9.25			
2,4-Dichloro-phenol	C ₆ H ₃ Cl ₂ OH	9.43			
Silicic acid	H ₄ SiO ₄	9.84	13.20		
Phenol	C ₆ H ₅ OH	9.98			
Cadmium ion	Cd ²⁺	10.08	10.27	12.95	14.05
Calcium ion	Ca ²⁺	12.60			

Mathematics of Acid/Base Speciation

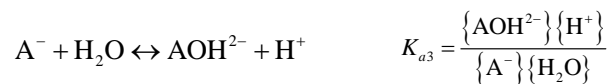
- Every acid/base group has a “core” that is unaltered as H⁺ or OH⁻ groups attach and detach. In a closed system in which the core participates only in acid/base reactions, its **total concentration (TOTC)** in solution remains constant, even when its distribution among acid/base species changes.

Consider a core A⁻ that can combine with H⁺ or OH⁻ to form H₂A⁺, HA, A⁻, or AOH²⁻. Then the **mass balance** on A in solution is:

$$TOTA = [H_2A^+] + [HA] + [A^-] + [AOH^{2-}]$$

Mathematics of Acid/Base Speciation

At equilibrium, each conjugate acid/base pair in a system must satisfy the equilibrium constant (K_a) for the corresponding reaction; i.e., in the example system:



Mathematics of Acid/Base Speciation

The equations characterizing the equilibrium speciation of A in terms of the concentrations of the A-containing species (and assuming that the standard state conc'n for solutes is 1.0 mol/L) are:

$$K_{a1} = \frac{\gamma_{HA} [HA] \gamma_{H^+} [H^+]}{\gamma_{H_2A^+} [H_2A^+]} \quad K_{a2} = \frac{\gamma_{A^-} [A^-] \gamma_{H^+} [H^+]}{\gamma_{HA} [HA]}$$

$$K_{a3} = \frac{\gamma_{AOH^{2-}} [AOH^{2-}] \gamma_{H^+} [H^+]}{\gamma_{A^-} [A^-]} (1.0)$$

$$TOTA = [H_2A^+] + [HA] + [A^-] + [AOH^{2-}]$$

Mathematics of Acid/Base Speciation

If $TOTA$, the K_a 's, and pH are known, and the activity coefficients can be estimated (e.g., from ionic strength), then we have four equations in four unknowns, which can be solved to determine the speciation. In the simplified case where the activity coefficients are all 1.0:

$$K_{a1} = \frac{(HA)(H^+)}{(H_2A^+)} \quad K_{a2} = \frac{(A^-)(H^+)}{(HA)}$$

$$K_{a3} = \frac{(AOH^{2-})(H^+)}{(A^-)}$$

$$TOTA = (H_2A^+) + (HA) + (A^-) + (AOH^{2-})$$

Mathematics of Acid/Base Speciation

- At equilibrium, all the K_a expressions and the mass balance on A can and must be satisfied independently; the fact that some of them contain identical terms (e.g., that the same species is an acid in one reaction and a conjugate base in another) does not alter this.
- The relationships are mathematical, not chemical. The results can be interpreted chemically, but the calculations can be carried out just like for any other set of algebraic equations.

Mathematics of Acid/Base Speciation

$$\frac{\{Acid\}}{\{Base\}} = \frac{\{H^+\}}{K_a} \quad \log \frac{\{Acid\}}{\{Base\}} = pK_a - pH$$

- The K_a expressions require that:
 - *Whenever the H^+ activity increases by a factor of x , the activity ratio of the acid to the conjugate base increases by this same factor*
 - *When H^+ activity equals K_a ($pH=pK_a$), the acid and base have equal activities*

Graphical Representation of Acid/Base Speciation

$$\log \frac{\{Acid\}}{\{Base\}} = pK_a - pH$$

