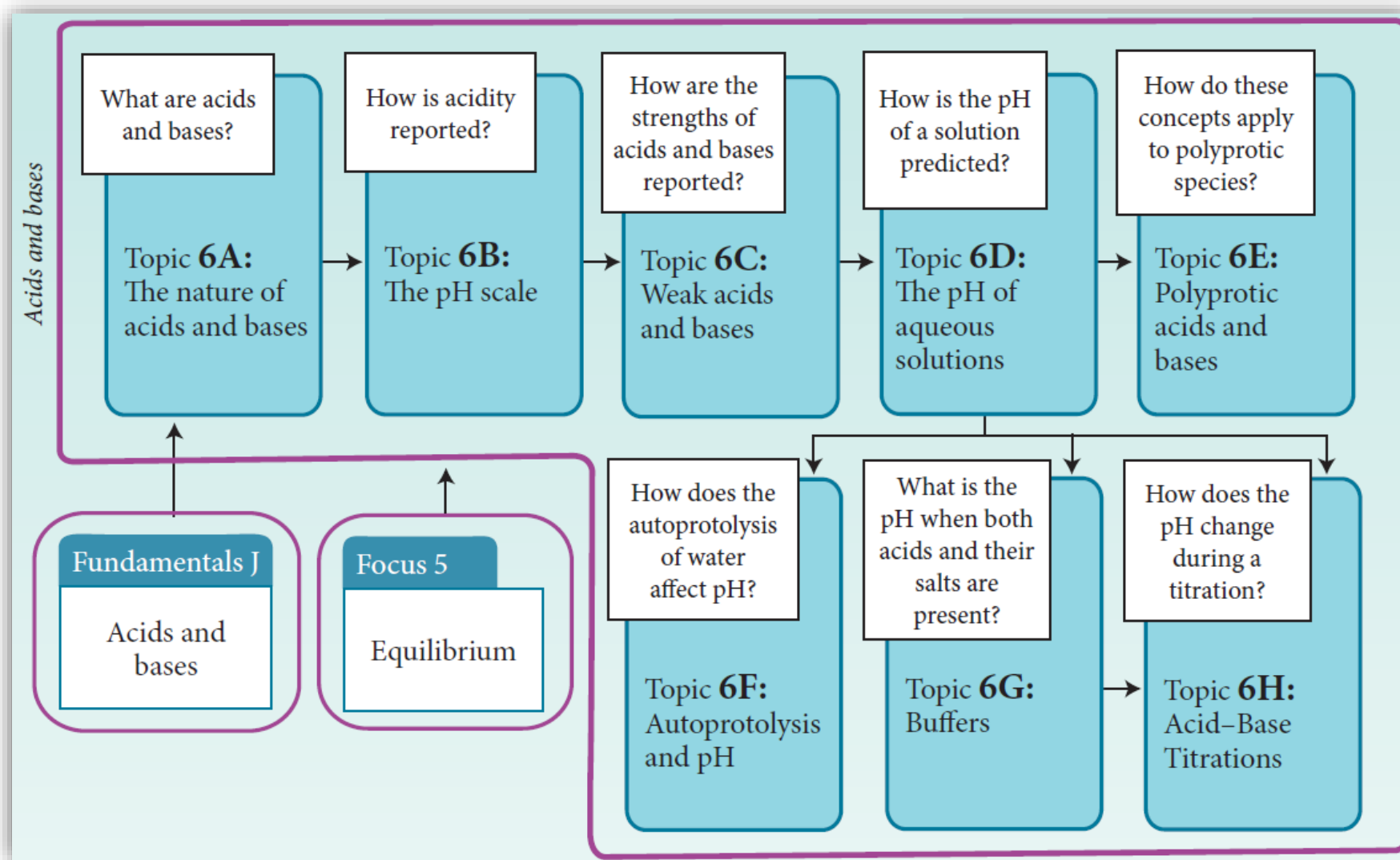
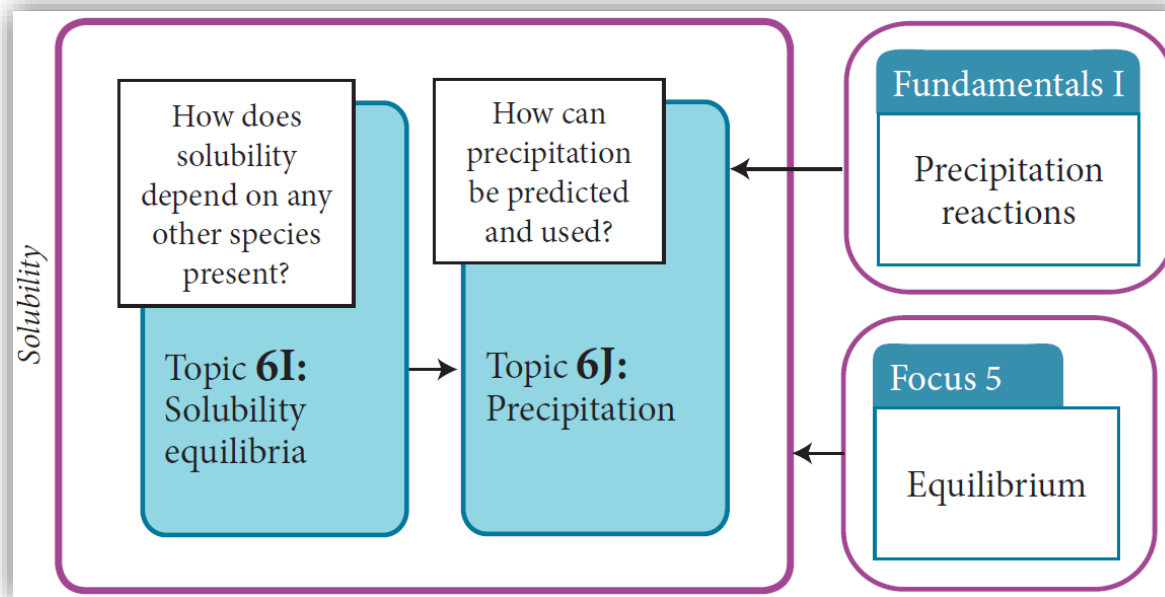


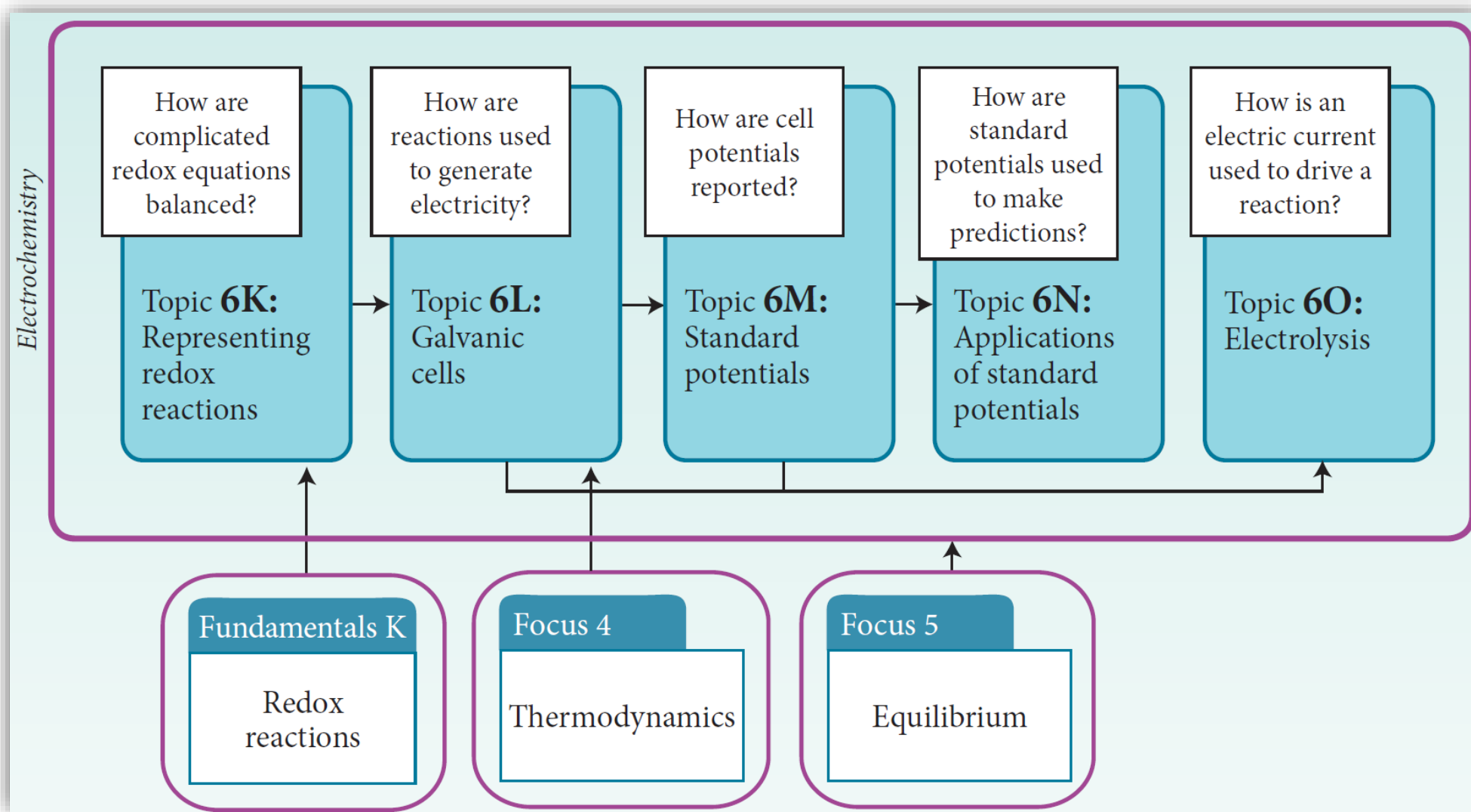
Focus 6. Reactions Overview



Focus 6. Reactions Overview



Focus 6. Reactions Overview



Topic 6A. The Nature of Acids and Bases

- 6A.1 Brønsted–Lowry Acids and Bases
- 6A.2 Lewis Acids and Bases
- 6A.3 Acidic, Basic, and Amphoteric Oxides
- 6A.4 Proton Exchange Between Water Molecules

Brønsted–Lowry Acids and Bases

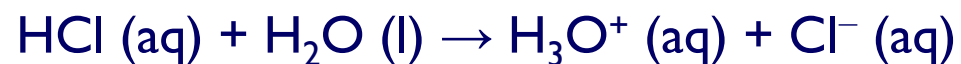
- Arrhenius definition (Fundamentals J)
 - Acid: a substance that dissociates in water to form H^+
 - Base: a substance that dissociates in water to form OH^-
- Brønsted-Lowry definition
 - Acid: proton donor
 - Base: proton acceptor

→ general theory for any solvent or even in absence of solvent

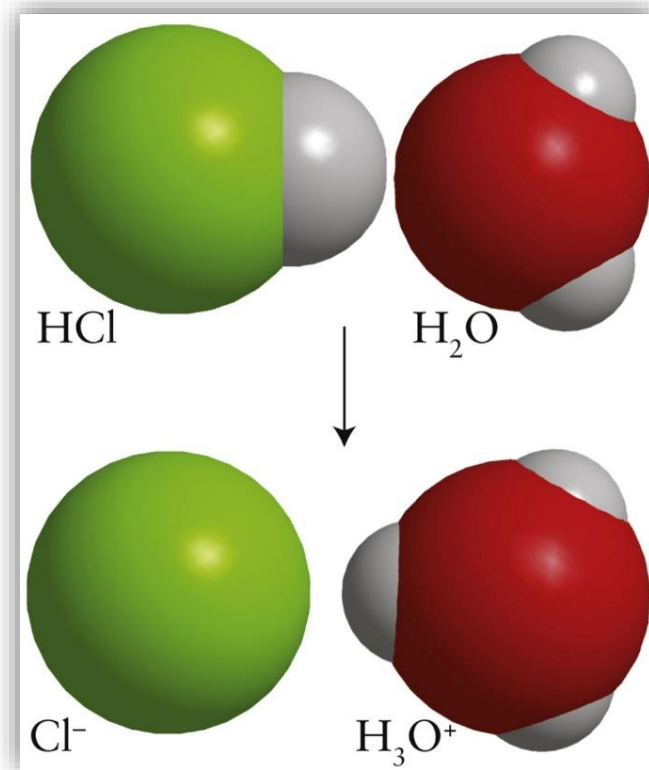
Brønsted–Lowry Acids and Bases

■ Strong/weak acid

- Strong acid: almost all the molecules are deprotonated in solution.

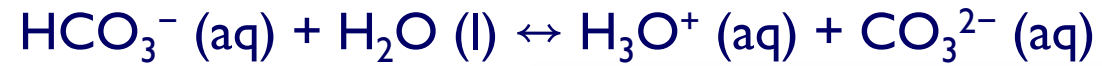


- Weak acid: only a small fraction of the molecules or ions are deprotonated in solution.



Brønsted–Lowry Acids and Bases

- Acid/Base reaction in nature



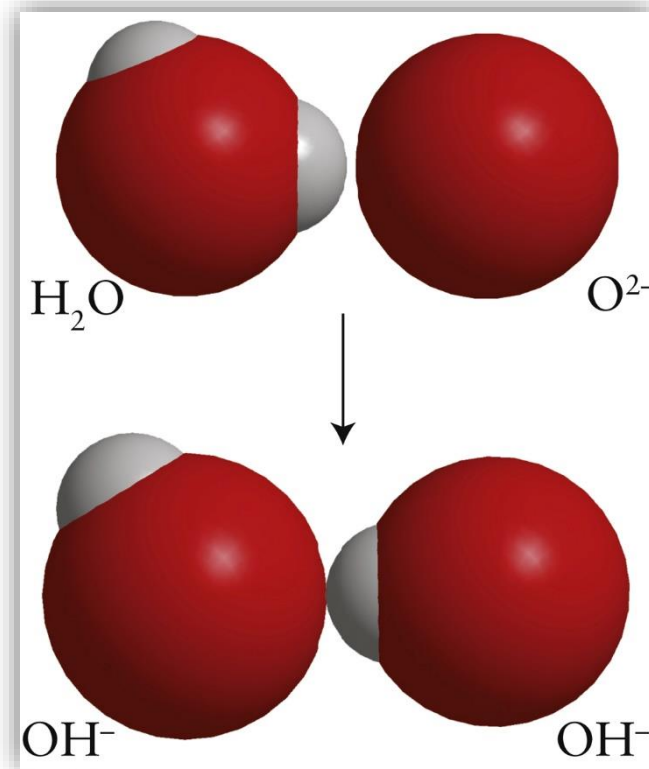
Brønsted–Lowry Acids and Bases

■ Strong/weak base

- Strong base: almost all the molecules are protonated in solution.

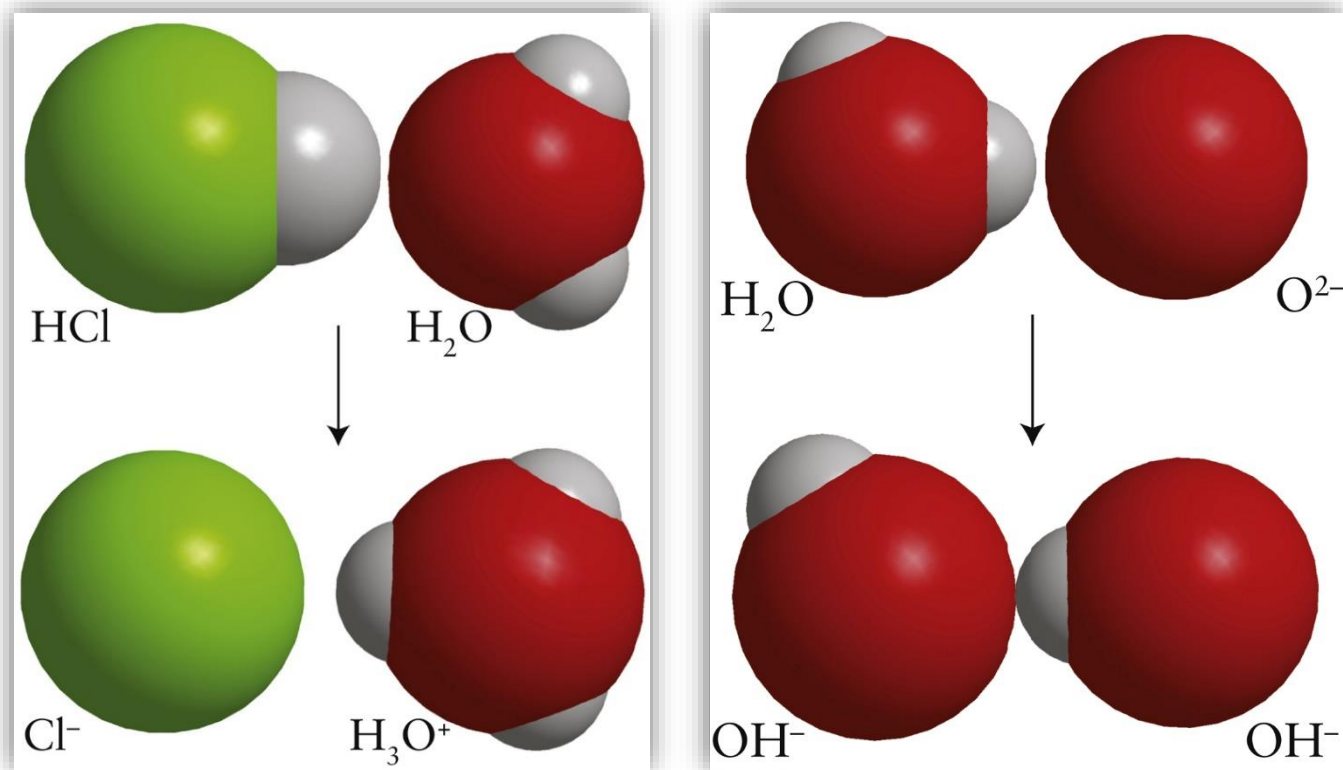


- Weak base: only a small fraction of the molecules or ions are protonated in solution.

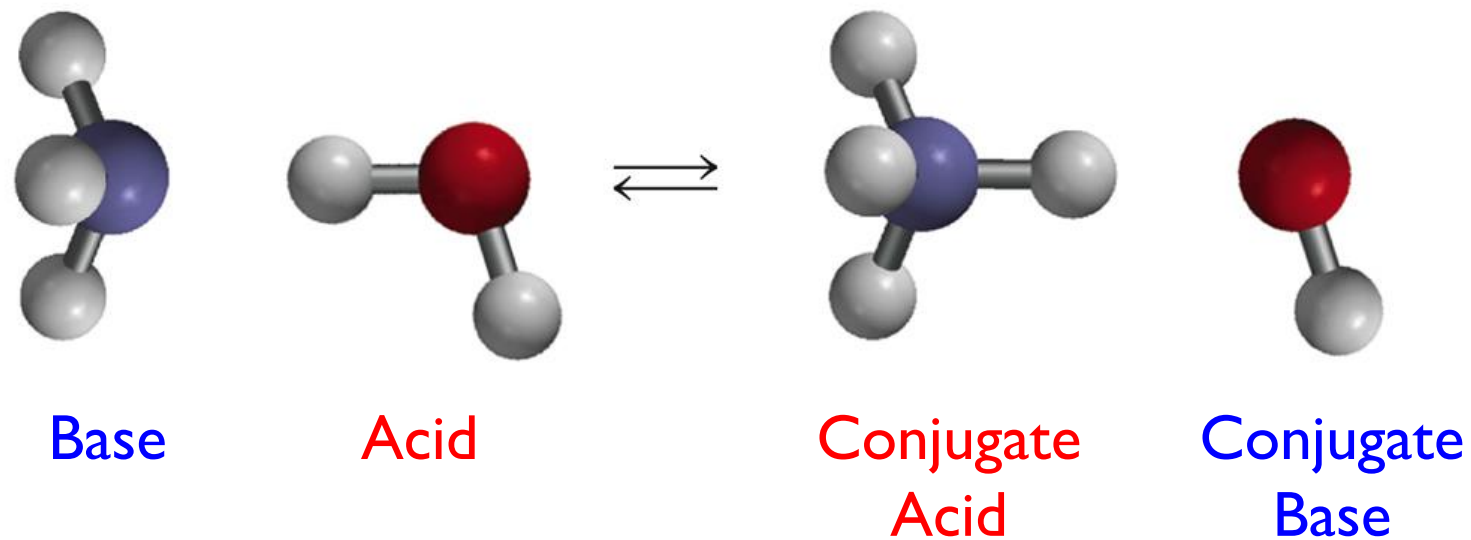
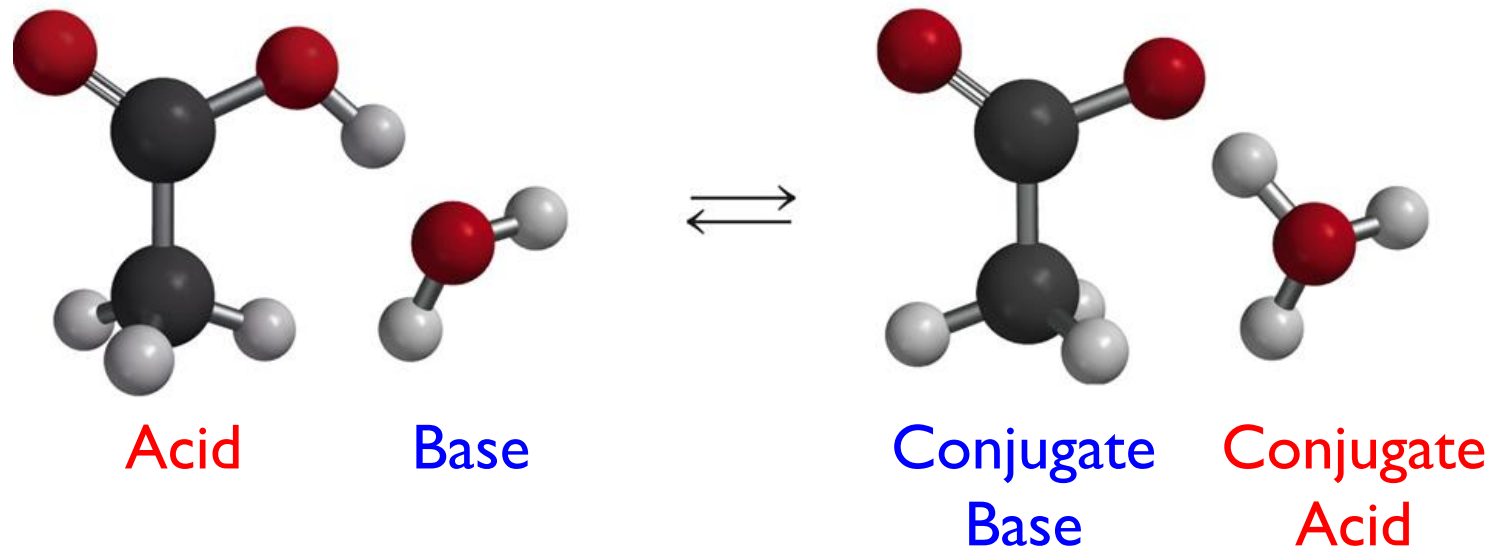


Brønsted–Lowry Acids and Bases

- Conjugate acid–base pair in proton transfer reactions.
 - Acid (proton donor) \rightarrow deprotonation \rightarrow conjugate base
 - Base (proton acceptor) \rightarrow protonation \rightarrow conjugate acid

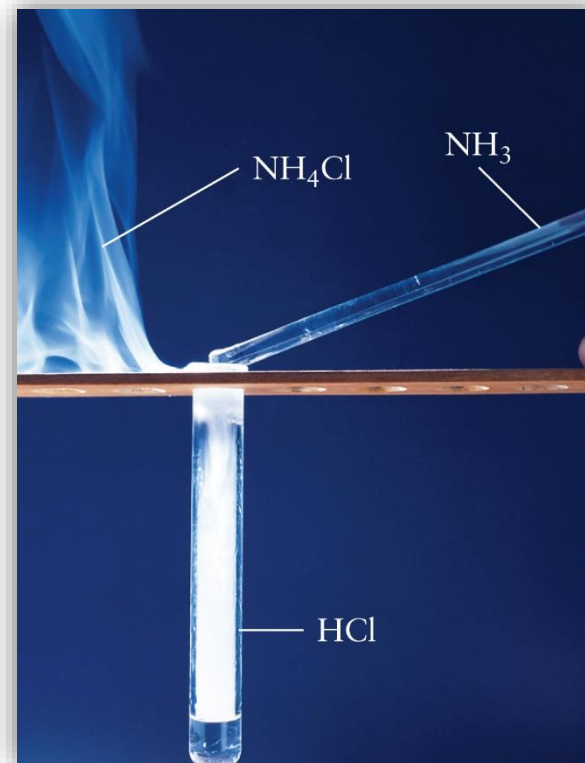


Brønsted–Lowry Acids and Bases



Brønsted–Lowry Acids and Bases

- The Brønsted definitions of acids and bases also apply to species in nonaqueous solvents and even to gas-phase reactions.



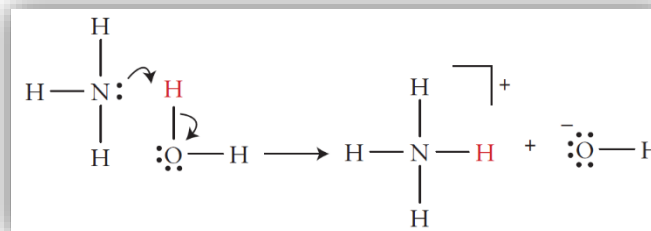
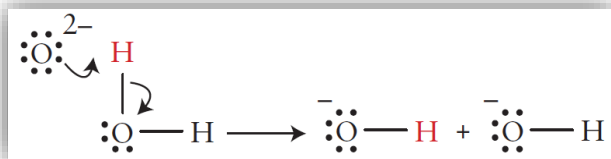
Lewis Acids and Bases

■ Lewis definition

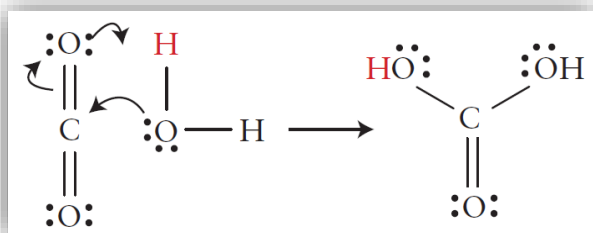
- **Acid:** electron pair acceptor
- **Base:** electron pair donor

■ More general than Brønsted-Lowry definition

- Ni(CO)_4 : Ni atoms (Lewis acid) + CO ligand (Lewis Base)
- $\text{O}^{2-} + \text{H}_2\text{O}$

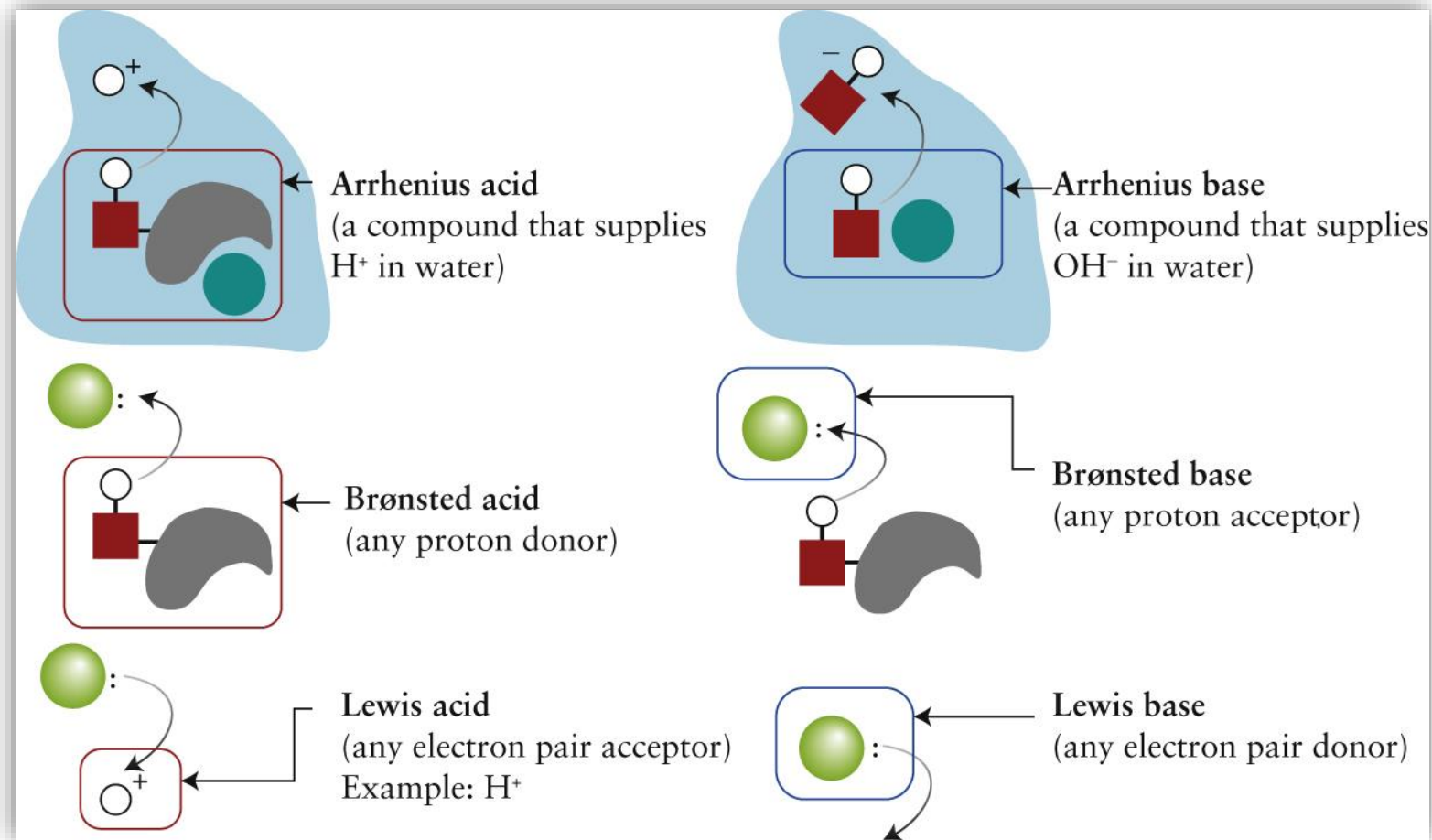


- $\text{CO}_2 + \text{H}_2\text{O}$



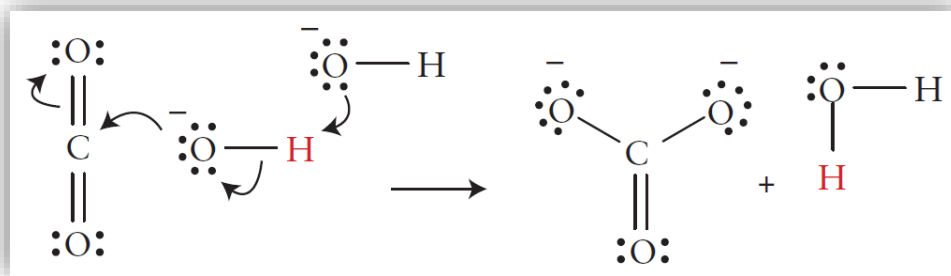
Lewis Acids and Bases

- Arrhenius vs Brønsted vs Lewis



Acidic, Basic, and Amphoteric Oxides

- **Acidic oxide:** an oxide that reacts with water to form a solution of Brønsted acid.
 - Non-metal molecules (CO_2 , SO_3 , Cl_2O_7 , N_2O_5 ...)
 - Generally, tend to act as Lewis acids and react with water to form a Brønsted acid (\rightarrow acidic oxide)
 - React with bases to form a salt and water
 - $2 \text{NaOH (aq)} + \text{CO}_2 \text{ (g)} \rightarrow \text{Na}_2\text{CO}_3 \text{ (aq)} + \text{H}_2\text{O (l)}$

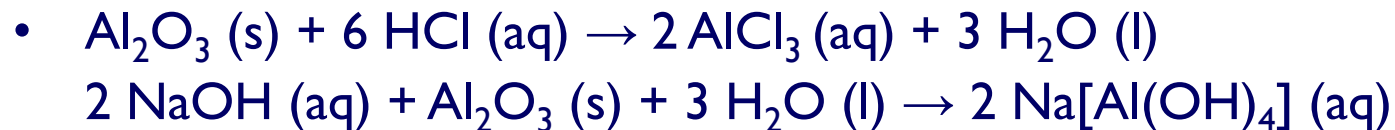












Acidic, Basic, and Amphoteric Oxides

- **Basic oxide:** an oxide that accepts protons from water to form a solution of hydroxide ions (Brønsted base).
 - Metal oxides (CaO, Na₂O, MgO ...)
 - Generally, tend to act as Lewis bases and react with water to form a Brønsted base
 - React with acids to form a salt and water
 - $\text{CaO (s)} + \text{H}_2\text{O (l)} \rightarrow \text{Ca(OH)}_2 \text{ (aq)}$
 $\text{MgO (s)} + 2 \text{HCl (aq)} \rightarrow \text{MgCl}_2 \text{ (aq)} + \text{H}_2\text{O (l)}$

Acidic, Basic, and Amphoteric Oxides

- **Amphoteric oxide:** an oxide that exhibits both acid and base characters and react with both acids and bases.



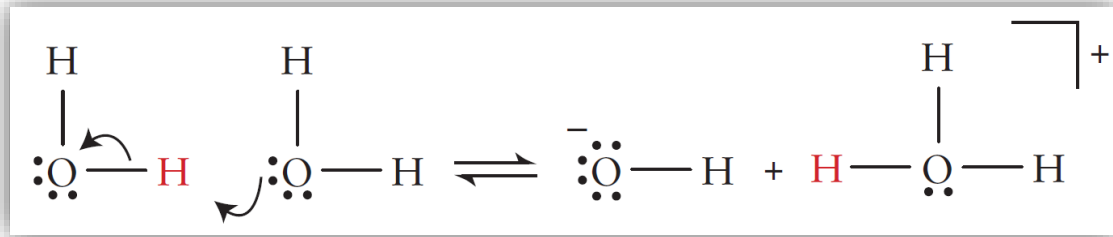
3	4	5	6	7	8	9	10	11	12
 +3 Sc	 +4 Ti	 +4 V	 +4 Cr	 +4 Mn	 +4, +3 Fe	 +3 Co	 +3 Ni	 +2 Cu	 +2 Zn

2	13	14	15	16
BeO	B			
	Al ₂ O ₃	Si		
	Ga ₂ O ₃	GeO ₂	As ₂ O ₃	
	In ₂ O ₃	SnO SnO ₂	Sb ₂ O ₃	Te
		PbO PbO ₂	Bi ₂ O ₃	Po

Proton Exchange between Water Molecules

- **Amphiprotic**

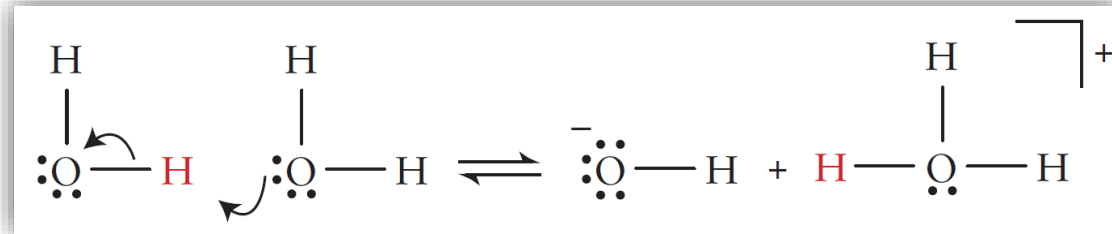
A molecule that can act both as a proton donor and as a proton acceptor.



Proton Exchange between Water Molecules

■ Authoprotolysis (autoionization)

- A reaction, in which one molecule transfers a proton to another molecule of the same kind.
- Amphiprotic species (H_2O , NH_3 ...) act as either a Brønsted acid (proton donor) or a Brønsted base (proton acceptor)



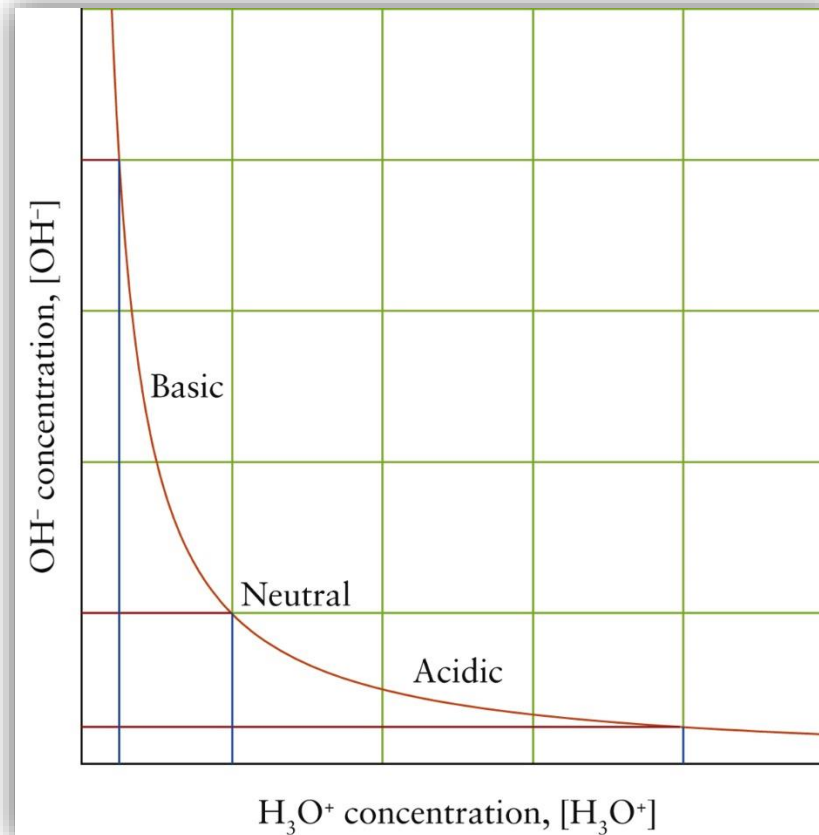
■ Autoionization constant, K_w

$$K_w = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{OH}^-}}{(a_{\text{H}_2\text{O}})^2} \approx [\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = 1.0 \times 10^{-14}$$

Proton Exchange between Water Molecules

- K_w is an equilibrium constant

The product of the concentrations of H_3O^+ and OH^- ions in any aqueous solution is always equal to K_w .



Topic 6B. The pH Scale

6B.1 The Interpretation of pH

6B.2 The pOH of Solutions

The Interpretation of pH

- pH scale: measure of acidity or basicity

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

For pure water,

$$\text{pH} = -\log (1.0 \times 10^{-7}) = 7.00$$

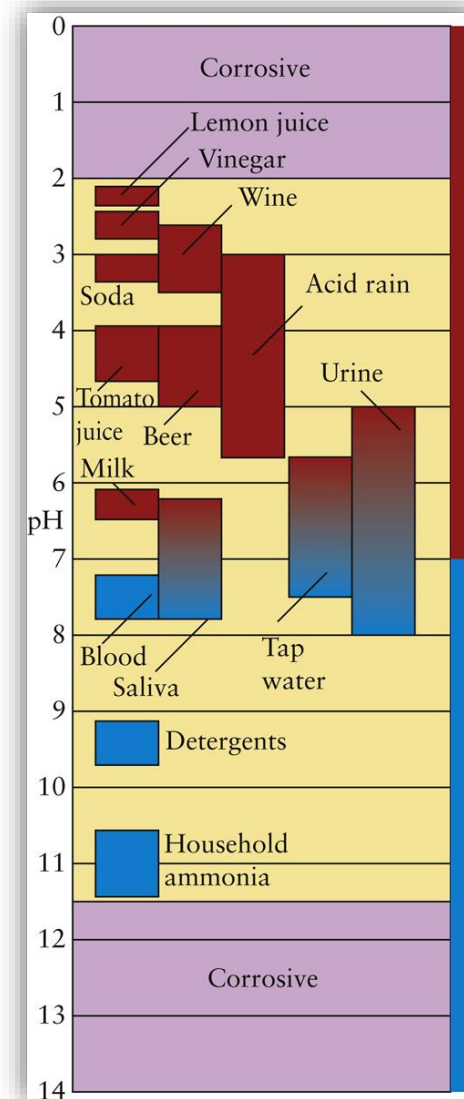


The Interpretation of pH

- Strong acids and bases \rightarrow reaction goes to almost completion



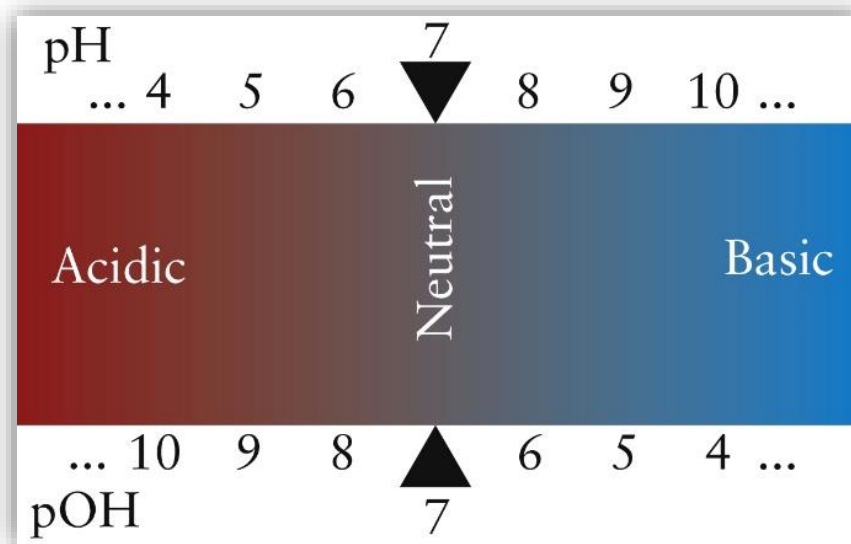
Thus,



The pOH of Solutions

- In general $pX = -\log X$
- $pOH = -\log a_{OH^-} = -\log [OH^-]$
- pK_w and pH-pOH in pure water

$$pK_w = -\log K_w = -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + -\log[OH^-] = pH + pOH = 14$$

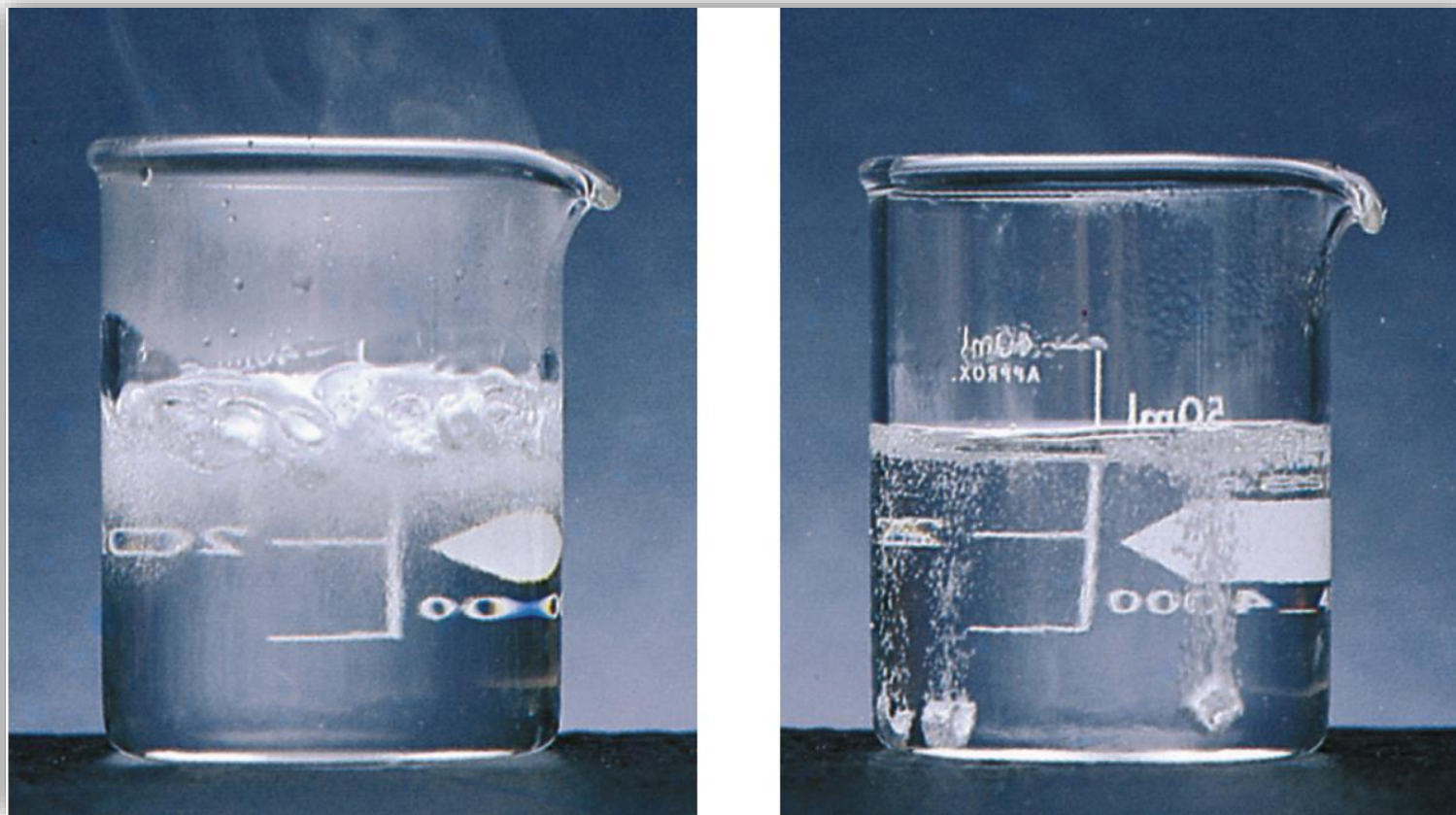


Topic 6C. Weak Acids and Bases

- 6C.1 Acidity and Basicity Constants
- 6C.2 The Conjugate Seesaw
- 6C.3 Molecular Structure and Acid Strength
- 6C.4 The Strengths of Oxoacids and Carboxylic Acids

Acidity and Basicity Constants

- Strong vs. weak acids



Acidity and Basicity Constants

- Weak acid



$$K = K_a = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}} \cdot a_{\text{H}_2\text{O}}} \approx \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \text{acidity constant}$$

$$\text{p}K_a = -\log K_a$$

TABLE 6C.1 Acidity Constants at 25 °C*

Acid	K_a	$\text{p}K_a$	Acid	K_a	$\text{p}K_a$
trichloroacetic acid, CCl_3COOH	3.0×10^{-1}	0.52	formic acid, HCOOH	1.8×10^{-4}	3.75
benzene sulfonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$	2.0×10^{-1}	0.70	benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$	6.5×10^{-5}	4.19
iodic acid, HIO_3	1.7×10^{-1}	0.77	acetic acid, CH_3COOH	1.8×10^{-5}	4.75
sulfurous acid, H_2SO_3	1.5×10^{-2}	1.81	carbonic acid, H_2CO_3	4.3×10^{-7}	6.37
chlorous acid, HClO_2	1.0×10^{-2}	2.00	hypochlorous acid, HClO	3.0×10^{-8}	7.53
phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12	hypobromous acid, HBrO	2.0×10^{-9}	8.69
chloroacetic acid, CH_2ClCOOH	1.4×10^{-3}	2.85	boric acid, B(OH)_3^\dagger	7.2×10^{-10}	9.14
lactic acid, $\text{CH}_3\text{CH(OH)COOH}$	8.4×10^{-4}	3.08	hydrocyanic acid, HCN	4.9×10^{-10}	9.31
nitrous acid, HNO_2	4.3×10^{-4}	3.37	phenol, $\text{C}_6\text{H}_5\text{OH}$	1.3×10^{-10}	9.89
hydrofluoric acid, HF	3.5×10^{-4}	3.45	hypoiodous acid, HIO	2.3×10^{-11}	10.64

*The values for K_a listed here have been calculated from $\text{p}K_a$ values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.

[†]The proton transfer equilibrium is $\text{B(OH)}_3(\text{aq}) + 2 \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{B(OH)}_4^-(\text{aq})$

Acidity and Basicity Constants

- Weak base



$$K = K_b = \frac{a_{\text{BH}^+} \cdot a_{\text{OH}^-}}{a_{\text{B}} \cdot a_{\text{H}_2\text{O}}} \approx \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \text{basicity constant}$$

$$\text{p}K_b = -\log K_b$$

TABLE 6C.2 Basicity Constants at 25 °C*

Base	K_b	$\text{p}K_b$	Base	K_b	$\text{p}K_b$
urea, $\text{CO}(\text{NH}_2)_2$	1.3×10^{-14}	13.90	ammonia, NH_3	1.8×10^{-5}	4.75
aniline, $\text{C}_6\text{H}_5\text{NH}_2$	4.3×10^{-10}	9.37	trimethylamine, $(\text{CH}_3)_3\text{N}$	6.5×10^{-5}	4.19
pyridine, $\text{C}_5\text{H}_5\text{N}$	1.8×10^{-9}	8.75	methylamine, CH_3NH_2	3.6×10^{-4}	3.44
hydroxylamine, NH_2OH	1.1×10^{-8}	7.97	dimethylamine, $(\text{CH}_3)_2\text{NH}$	5.4×10^{-4}	3.27
nicotine, $\text{C}_{10}\text{H}_{14}\text{N}_2$	1.0×10^{-6}	5.98	ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$	6.5×10^{-4}	3.19
morphine, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$	1.6×10^{-6}	5.79	triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$	1.0×10^{-3}	2.99
hydrazine, NH_2NH_2	1.7×10^{-6}	5.77			

*The values for K_b listed here have been calculated from $\text{p}K_b$ values with more significant figures than shown so as to minimize rounding errors.

Acidity and Basicity Constants

- 1 M of acetic acid in water
 - $K_a = 1.75 \times 10^{-5}$ or $pK_a = -\log K_a = 4.757$

What are the equilibrium pressures of the products and reactants?

	AcH	Ac-	H+
Initial	1	0	0
Change	$-x$	x	x
Equilibrium	$1 - x$	x	x

$$K_a = \frac{[Ac^-][H^+]}{[AcH]} = \frac{x^2}{1-x} = 1.75 \times 10^{-5}$$

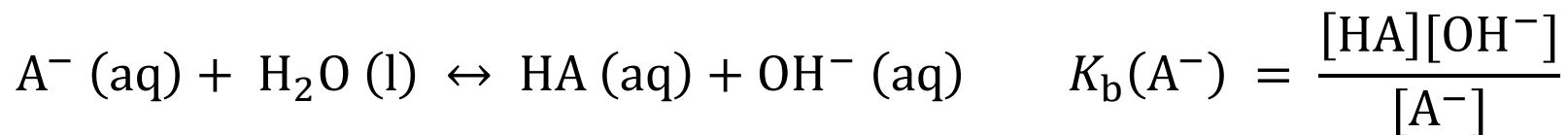
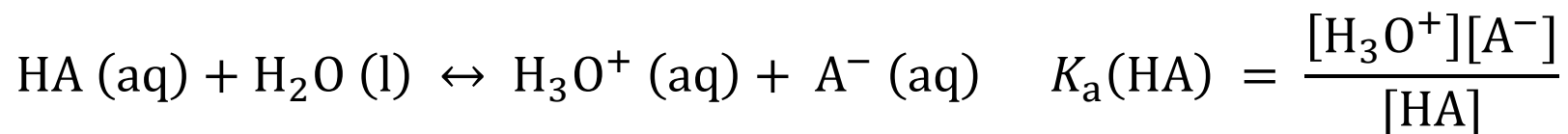
K_a is small $\rightarrow x \ll 1, 1 - x \approx 1$

$$\therefore x^2 = 1.75 \times 10^{-5}, x = \sqrt{1.75 \times 10^{-5}} = 0.00418 \text{ M}$$

Conjugate Seesaw

■ Conjugate seesaw

- The stronger the acid, the weaker is its conjugate base.
- The stronger the base, the weaker is its conjugate acid.



$$\text{p}K_a(\text{HA}) + \text{p}K_b(\text{A}^-) = \text{p}K_w = \text{const.}$$

	$\text{p}K_a$	$\text{p}K_b$	
	2.00	12.00	Chlorous acid
	4.75	9.25	Acetic acid
	7.53	6.47	Hypochlorous acid
Ammonia	9.25	4.75	
Methylamine	10.56	3.44	

Conjugate Seesaw

TABLE 6C.3 Conjugate Acid–Base Pairs Arranged by Strength

pK _a	Acid name	Acid formula	Base formula	Base name	pK _b
	Strong acid			Very weak base	
	hydroiodic acid	HI	I [−]	iodide ion	
	perchloric acid	HClO ₄	ClO ₄ [−]	perchlorate ion	
	hydrobromic acid	HBr	Br [−]	bromide ion	
	hydrochloric acid	HCl	Cl [−]	chloride ion	
	sulfuric acid	H ₂ SO ₄	HSO ₄ [−]	hydrogen sulfate ion	
	chloric acid	HClO ₃	ClO ₃ [−]	chlorate ion	
	nitric acid	HNO ₃	NO ₃ [−]	nitrate ion	
	hydronium ion	H ₃ O ⁺	H ₂ O	water	
1.92	hydrogen sulfate ion	HSO ₄ [−]	SO ₄ ^{2−}	sulfate ion	12.08
3.37	nitrous acid	HNO ₂	NO ₂ [−]	nitrite ion	10.63
3.45	hydrofluoric acid	HF	F [−]	fluoride ion	10.55
4.75	acetic acid	CH ₃ COOH	CH ₃ CO ₂ [−]	acetate ion	9.25
6.37	carbonic acid	H ₂ CO ₃	HCO ₃ [−]	hydrogen carbonate ion	7.63
6.89	hydrosulfuric acid	H ₂ S	HS [−]	hydrogen sulfide ion	7.11
9.25	ammonium ion	NH ₄ ⁺	NH ₃	ammonia	4.75
9.31	hydrocyanic acid	HCN	CN [−]	cyanide ion	4.69
10.25	hydrogen carbonate ion	HCO ₃ [−]	CO ₃ ^{2−}	carbonate ion	3.75
10.56	methylammonium ion	CH ₃ NH ₃ ⁺	CH ₃ NH ₂	methylamine	3.44
	water	H ₂ O	OH [−]	hydroxide ion	
	ammonia	NH ₃	NH ₂ [−]	amide ion	
	hydrogen	H ₂	H [−]	hydride ion	
	methane	CH ₄	CH ₃ [−]	methide ion	
	hydroxide ion	OH [−]	O ^{2−}	oxide ion	
	Very weak acid			Strong base	

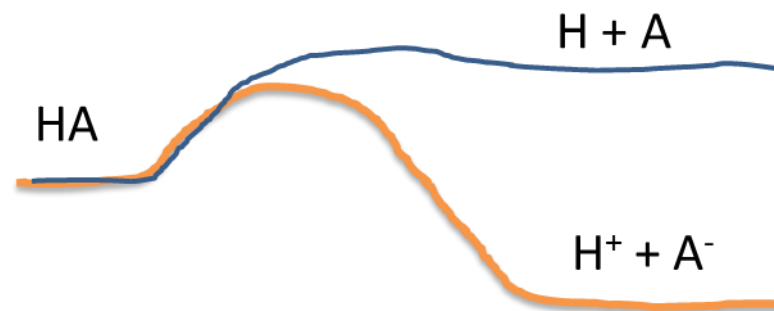
Molecular Structure and Acid Strength

- Relative acidity

- Gibbs free energy ($\Delta G_r^\circ = -RT \ln K$): the breaking of the H–A
- Solvent: the formation of an $\text{H}_2\text{O}–\text{H}^+$

- Strong acids have

- Unstable HA (aq)
- Unstable A (aq)
- Stable A^- (aq)
- Weak H–A bond
- Strong ionic character



Molecular Structure and Acid Strength

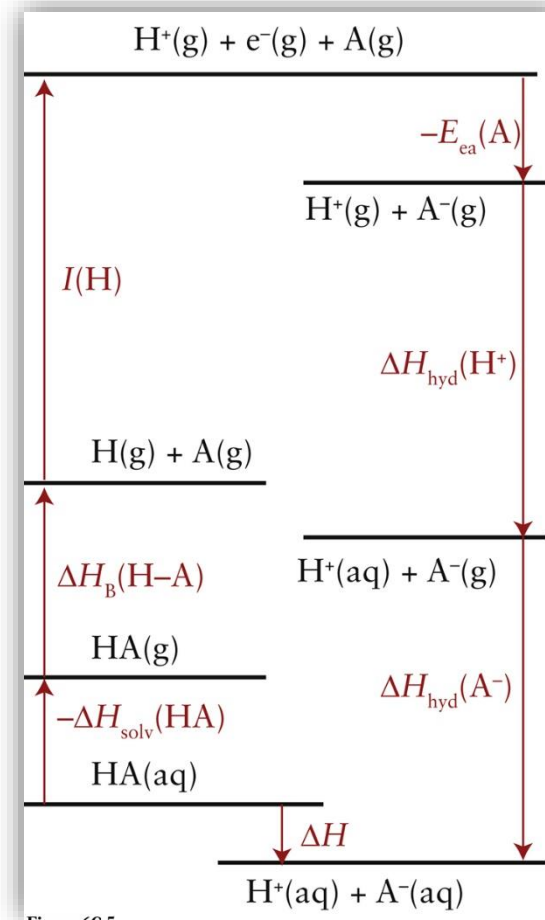
- Consider the thermodynamics of $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$

Step	Reaction	Enthalpy change
Removal of HA from solution:	$\text{HA(aq)} \rightarrow \text{HA(g)}$	$-\Delta H_{\text{solv}}(\text{HA})$
Dissociation of gaseous HA:	$\text{HA(g)} \rightarrow \text{H(g)} + \text{A(g)}$	$\Delta H_{\text{B}}(\text{H}-\text{A})$
Ionization of H:	$\text{H(g)} \rightarrow \text{H}^+(\text{g}) + \text{e}^-(\text{g})$	$I(\text{H})$
Electron attachment to A:	$\text{A(g)} + \text{e}^-(\text{g}) \rightarrow \text{A}^-(\text{g})$	$-E_{\text{ea}}(\text{A})$
Hydration of H^+ :	$\text{H}^+(\text{g}) + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq})$	$\Delta H_{\text{hyd}}(\text{H}^+)$
Hydration of A^- :	$\text{A}^-(\text{g}) \rightarrow \text{A}^-(\text{aq})$	$\Delta H_{\text{hyd}}(\text{A}^-)$

TABLE 6C.4 Contributions to the Enthalpy of Proton Transfer of Binary Acids*

Acid	$\Delta H_{\text{solv}}(\text{HA})$	$\Delta H_{\text{B}}(\text{H}-\text{A})$	$I(\text{H})$	$E_{\text{ea}}(\text{A})$	$\Delta H_{\text{hyd}}(\text{H}^+)$	$\Delta H_{\text{hyd}}(\text{A}^-)$	ΔH
NH_3	-34	453	1312	71	-1103	-500	+125
H_2O	-41	492	1312	178	-1103	-520	+44
HF	-49	565	1312	328	-1103	-510	-15
HCl	? -35	431	1312	349	-1103	-367	-41
HBr	? -35	366	1312	325	-1103	-336	-51
HI	? -35	299	1312	295	-1103	-291	-43

*(All values in kilojoules per mole ($\text{kJ}\cdot\text{mol}^{-1}$). Grayed-out values are contributions that are constant for all the acids. The colors are explained in the text. The values preceded with ? are estimates. Note that NH_3 is functioning as an acid (a proton donor) in this context.




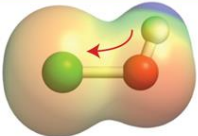

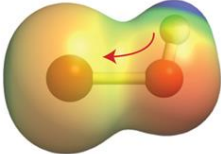

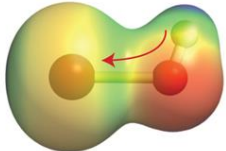
Molecular Structure and Acid Strength

- Electron affinity
 - In HA, the greater the electron affinity (and therefore the electronegativity) of A, the stronger the acidity.
 - $\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$
- Bond strength
 - Weaker the H–A bond, stronger the acidity.
 - $\text{HF} \ll \text{HCl} < \text{HBr} < \text{HI}$
 $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$

The Strengths of Oxoacids and Carboxylic Acids

- Oxoacids: A–O–H (A = halogen)
 - The greater the electronegativity of the halogen, the stronger is the oxoacid
 - Acidity: $\text{HClO} > \text{HBrO} > \text{HIO}$

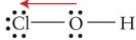
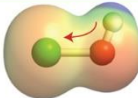
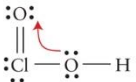
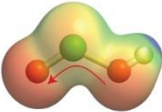
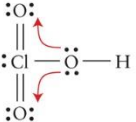
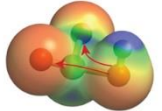
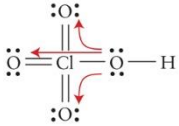
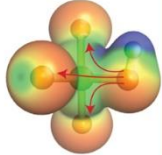
TABLE 6C.5 Correlation of Acid Strength and Electronegativity

Acid, HAO	Structure*	Electronegativity of atom A	$\text{p}K_{\text{a}}$	
hypochlorous acid, HClO		3.2	7.53	
hypobromous acid, HBrO		3.0	8.69	
hypoiodous acid, HIO		2.7	10.64	

The Strengths of Oxoacids and Carboxylic Acids

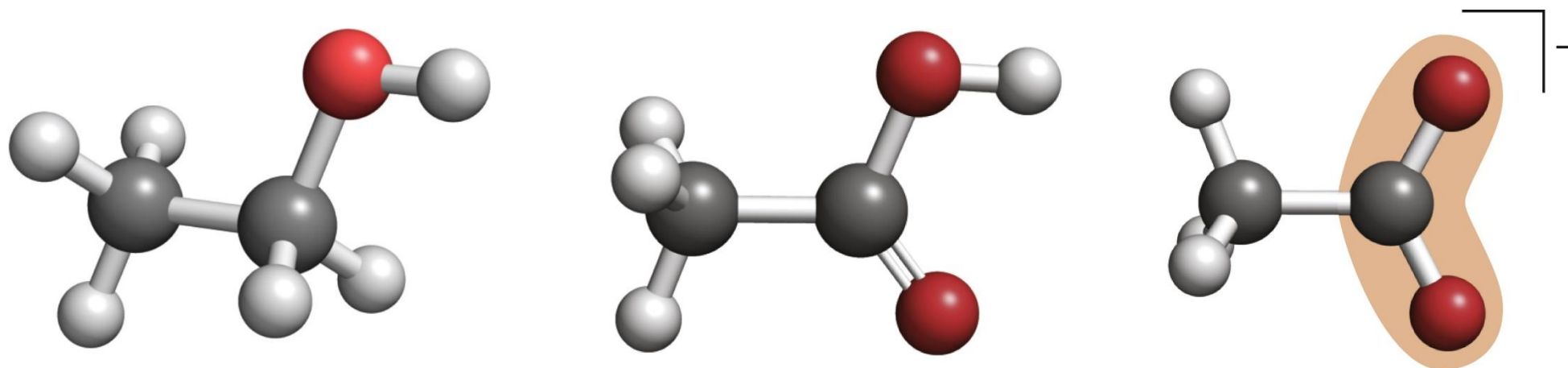
- For $A-O_x-H$
 - The greater the number of oxygen atoms attached to the central atom (or the oxidation number of A), the stronger is the acid
 - Acidity: $HClO < HClO_2 < HClO_3 < HClO_4$

TABLE 6C.6 Correlation of Acid Strength and Oxidation Number

Acid	Structure*	Oxidation number of Cl atom	pK_a	
hypochlorous acid, $HClO$		+1	7.53	
chlorous acid, $HClO_2$		+3	2.00	
chloric acid, $HClO_3$		+5	strong	
perchloric acid, $HClO_4$		+7	strong	

The Strengths of Oxoacids and Carboxylic Acids

- Carboxylic group
 - Structurally similar to alcohols but they show significant acidity because of **resonance stabilization** of carboxylate anions, as well as the presence of additional oxygen .



The Strengths of Oxoacids and Carboxylic Acids

TABLE 6C.7 Correlations of Molecular Structure and Acid Strength*

Acid type	Trend	
binary	The more polar the H—A bond, the stronger the acid. <i>This effect is dominant for acids of the same period.</i>	
	The weaker the H—A bond, the stronger the acid. <i>This effect is dominant for acids of the same group.</i>	
oxoacid	The greater the number of O atoms attached to the central atom (the greater the oxidation number of the central atom), the stronger the acid.	
	For the same number of O atoms attached to the central atom, then the greater the electronegativity of the central atom, the stronger the acid.	
carboxylic	The greater the electronegativities of the groups attached to the carboxyl group, the stronger the acid.	