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Department of Chemistry

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Chapter 4. Acids and bases

Chapter 5. Acids and bases

Definitions of acids and bases: **Arrhenius,** Bronsted acidity, **Lewis**
Arrhenius
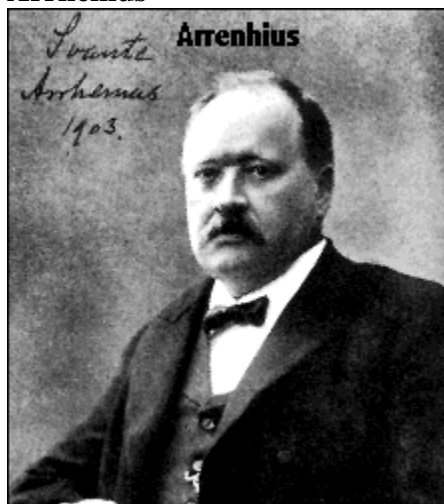
acid: generates $[H^+]$ in solution
base: generates $[OH^-]$ in solution
normal Arrhenius equation: acid + base <---> salt + water
example: $HCl + NaOH$ <---> $NaCl + H_2O$
Bronsted-Lowery:The Brønsted/Lowry Defintions specifies an acid as a proton donor and a base as a proton acceptor which applies to aqueous systems.
 The General Solvent System Definition is an extension to any autoionizing solvent. An acid is defined as a substance increasing the concentration of the characteristic cation of the solvent. One that increases the concentration of the characteristic anion (or decreases the concentrqtion of the cation) is a base.
acid: anything that donates a $[H^+]$ (proton donor)
base: anything that accepts a $[H^+]$ (proton acceptor)
normal Bronsted-Lowery equation: acid + base <---> acid + base
example: $HNO_2 + H_2O$ <---> $NO_2^- + H_3O^+$
Each acid has a conjugate base and each base has a conjugate acid. These conjugate pairs only differ by a proton. In this example: HNO_2 is the acid, H_2O is the base, NO_2^- is the conj. base, and H_3O^+ is the conj. acid.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

HCl is an acid
NaOH and Na_2O are bases

$2H_3N \rightleftharpoons NH_4^+ + NH_2^-$
NH_4Cl or urea, $H_2N(CO)NH_2$ are acids
$NaNH_2$ and Na_2N are bases
$2NO_2 \rightleftharpoons NO^+ + NO_3^-$
NOCl is an acid
$NaNO_3$ is a base
$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$ CH_3COOH is an actually a base which is protonated to $CH_3COOH_2^+$
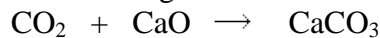$HAsF_6$ might be an acid if it does not react.
$NaHSO_3$ is a base
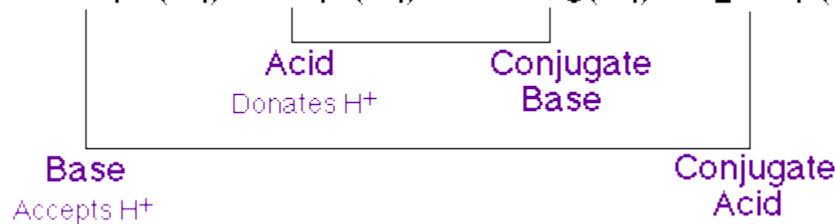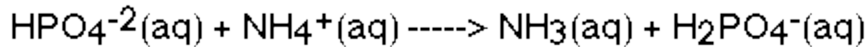
5.5 Anhydrous oxides
The Lux/Flood Definition
Covers things which would become acids or bases if dissolved in water.
$CO_2 + CaO \longrightarrow CaCO_3$
Here CO_2 is considered the acid - carbonic acid anhydride and CaO is considered the base since it woud give $Ca(OH)_2$ in water.
 The Lux/Flood definition defines an acid as an oxide ion acceptor and a base as an oxide ion donor and is mainly used for high temperature anhydrous systems for example in steel-making (in acidic or basic "slags"):
$CaO + SiO_2 \longrightarrow CaSiO_3$
$2Na_2O + P_2O_5 \rightleftharpoons 2Na_3PO_4$
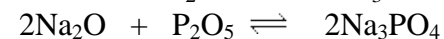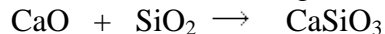
Aicd Bases in Water

5.1 Proton transfer equilibria in water
We typically talk about acid-base reactions in aqueous-phase environments -- that is, in the presence of water. The most fundamental acid-base reaction is the dissociation of water:

$$H_2O \longleftrightarrow H^+ + OH^-$$
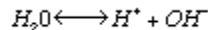
In this reaction, water breaks apart to form a hydrogen ion (H^+) and a hydroxyl ion (OH^-). In pure water, we can define a special equilibrium constant (K_w) as follows:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

Where K_w is the equilibrium constant for water (unitless)
$[H^+]$ is the molar concentration of hydrogen
$[OH^-$ is the molar concentration of hydroxide

An equilibrium constant less than one (1) suggests that the reaction prefers to stay on the side of the reactants -- in this case, water likes to stay as water. Because water hardly ionizes, it is a very poor conductor of electricity.

pH

What is of interest in this reading, however, is the acid-base nature of a substance like water. Water actually behaves both like an acid and a base. The acidity or basicity of a substance is defined most typically by the pH value, defined as below:

$$pH = -\log[H^+]$$

At equilibrium, the concentration of H^+ is 10^{-7}, so we can calculate the pH of water at equilbrium as:

$$pH = -\log[H^+] = -\log[10^{-7}] = 7$$

Solutions with a pH of seven (7) are said to be neutral, while those with pH values below seven (7) are defined as acidic and those above pH of seven (7) as being basic.

pOH gives us another way to measure the acidity of a solution. It is just the opposite of pH. A high pOH means the solution is acidic while a low pOH means the solution is basic.

$$pOH = -\log[OH^-]$$
$$pH + pOH = 14.00$$

Salts

A salt is formed when an acid and a base are mixed and the acid releases H^+ ions while the base releases OH^- ions. This process is called hydrolysis. The pH of the salt depends on the strengths of the original acids and bases:

Acid	Base	Salt pH
strong	strong	pH = 7
weak	strong	pH > 7
strong	weak	pH < 7
weak	weak	depends on which is stronger

This is because the conjugate base of a strong acid is very weak and cannot undergo hydrolysis. Similarily, the conjugate acid of a strong base is very weak and likewise does not undergo hydrolysis.

Acid-Base Character

For a molecule with a H-X bond to be an acid, the hydrogen must have a positive oxidation number so it can ionize to form a positive +1 ion. For instance, in sodium hydride (NaH) the

hydrogen has a -1 charge so it is not an acid but it is actually a base. Molecules like CH_4 with nonpolar bonds also cannot be acids because the H does not ionize. Molecules with strong bonds (large electronegativity differences), are less likely to be strong acids because they do not ionize very well. For a molecule with an X-O-H bond (also called an oxyacid) to be an acid, the hydrogen must again ionize to form H^+. To be a base, the O-H must break off to form the hydroxide ion (OH⁻). Both of these happen when dealing with oxyacids.

Strong Acids: These acids completely ionize in solution so they are always represented in chemical equations in their ionized form. There are only seven (7) strong acids:

$$HCl, HBr, HI, H_2SO_4, HNO_3, HClO_3, HClO_3, HClO_4$$

To calculate a pH value, it is easiest to follow the standard "Start, Change, Equilibrium" process.

Example Problem: Determine the pH of a 0.25 M solution of HBr.
Answer:

	HBr (aq)	→	H^+(aq)	+	Br⁻(aq)
Start	.25 M		0 M		0 M
Change	-.25		+.25		+.25
Equilibrium	0		.25		.25

$pH = -log[H^+] = -log(.25) = 0.60$

Weak Acids: These are the most common type of acids. They follow the equation:

$$HA(aq) <---> H^+(aq) + A^-(aq)$$
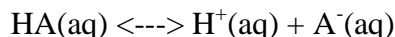
The equilibrium constant for the dissociation of an acid is known as K_a. The larger the value of K_a, the stronger the acid.

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

Example Problem: Determine the pH of .30 M acetic acid ($HC_2H_3O_2$) with the Ka of $1.8x10^{-5}$.
Answer:

Write the equlibrium equation for the acid :
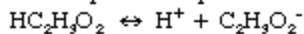
$$HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2^-$$

Write the equlibrium expression and the Ka value :

$$Ka = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8x10^{-5}$$

"Start, Change, Equilibrium":

	$HC_2H_3O_2$	↔	H^+	+	$C_2H_3O_2^-$
Start	0.30 M		0 M		0 M
Change	- x		+x		+x
Equilibrium	0.30 - x		x		x

Substitute the variables (disregard the "-x" because it is so small compared to the 0.30) and solve for $[H^+]$:

$$Ka = 1.8x10^{-5} = \frac{(x)(x)}{(.30 - x)} = \frac{x^2}{.30}$$

$$x = [H^+] = 2.3x10^{-3}$$

$$pH = -log[H^+] = 2.64$$

Strong Bases: Like strong acids, these bases completely ionize in solution and are always represented in their ionized form in chemical equations. There are only seven (7) strong bases:

$$LiOH, NaOH, KOH, RbOH, Ca(OH)_2, Sr(OH)_2, Ba(OH)_2$$
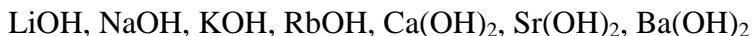
Example Problem: Determine the pH of a 0.010 M solution of $Ba(OH)_2$.

Answer:

	$Ba(OH)_2$ (aq)	→	Ba^{2+}(aq)	+	$2OH^-$ (aq)
Start	.010 M		0 M		0 M
Change	-.010		+.010		+.010
Equilibrium	0		.010		.010

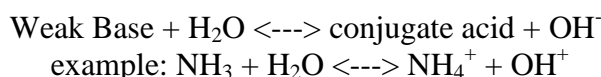$pOH = -\log[OH^-] = -\log(.010) = 1.70$
$pH = 14.00 - 1.70 = 12.30$

Weak Bases: They follow the equation:

$$Weak\ Base + H_2O <---> conjugate\ acid + OH^-$$
$$example:\ NH_3 + H_2O <---> NH_4^+ + OH^+$$

K_b is the base-dissociation constant:

$$K_b = \frac{[conjugate\ acid\,][OH^-]}{[weak\ base\,][H_2O]}$$

$$example:\ K_b = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]}$$

$$K_a\ x\ K_b = K_w = 1.00x10^{-14}$$

To calculate the pH of a weak base, we must follow a very similar "Start, Change, Equilibrium" process as we did with the weak acid, however we must add a few steps.

Example Problem: Determine the pH of 0.15 M ammonia (NH_3) with a $Kb=1.8x10^{-5}$.

Answer:

Write the equlibrium equation for the base :
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

Write the equlibrium expression and the Kb value :
$$Kb = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} = 1.8x10^{-5}$$

"Start, Change, Equilibrium":

	NH_3	+	H_2O	$\leftrightarrow$	NH_4^+	+	OH^-
Start	0.15 M		--		0 M		0 M
Change	-x		--		+x		+x
Equilibrium	0.15-x		--		x		x

Substitute the variables (disregard the "-x" because it is so small compared to the 0.15) and solve for [OH⁻]:

$$Kb = 1.8x10^{-5} = \frac{(x)(x)}{(.15-x)} = \frac{x^2}{.15}$$
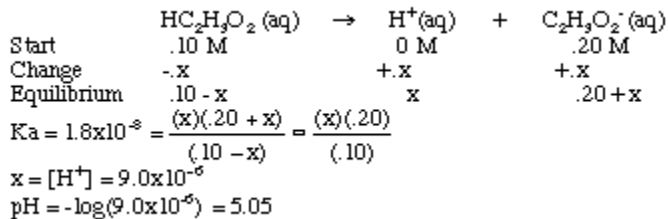
$x = [OH^-] = 1.6x10^{-3}$ M
$pOH = -\log[OH^-] = 2.80$
$pH = 14.00 - 2.80 = 11.20$

When dealing with weak acids and weak bases, you also might have to deal with the "common ion effect". This is when you add a salt to a weak acid or base which contains one of the ions

present in the acid or base. To be able to use the same process to solve for pH when this occurs, all you need to change are your "start" numbers. Add the molarity of the ion which comes from the salt and then solve the K_a or K_b equation as you did earlier.
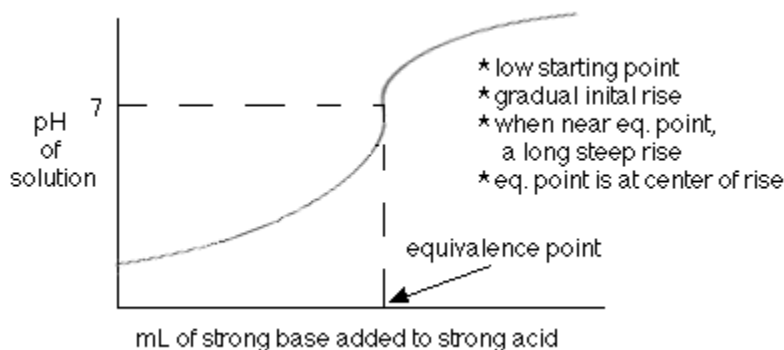
Example Problem: Find the pH of a solution formed by dissolving 0.100 mol of $HC_2H_3O_2$ with a Ka of 1.8×10^{-8} and 0.200 mol of $NaC_2H_3O_2$ in a total volume of 1.00 L.

Answer:

$$HC_2H_3O_2 \text{ (aq)} \rightarrow H^+\text{(aq)} + C_2H_3O_2^- \text{ (aq)}$$

	$HC_2H_3O_2$	H^+	$C_2H_3O_2^-$
Start	.10 M	0 M	.20 M
Change	-.x	+.x	+.x
Equilibrium	.10 - x	x	.20 + x

$$Ka = 1.8 \times 10^{-8} = \frac{(x)(.20 + x)}{(.10 - x)} = \frac{(x)(.20)}{(.10)}$$

$$x = [H^+] = 9.0 \times 10^{-6}$$

$$pH = -\log(9.0 \times 10^{-6}) = 5.05$$

Acid-Base Titrations

An acid-base titration is when you add a base to an acid until the equivalence point is reached which is where the moles of acid equals the moles of base. For the titration of a strong base and a strong acid, this equivalence point is reached when the pH of the solution is seven (7) as seen on the following titration curve:

pH of solution

7

* low starting point
* gradual inital rise
* when near eq. point, a long steep rise
* eq. point is at center of rise

equivalence point

mL of strong base added to strong acid

For the titration of a strong base with a weak acid, the equivalence point is reached when the pH is greater than seven (7). The half equivalence point is when half of the total amount of base needed to neutralize the acid has been added. It is at this point where the pH = pK_a of the weak acid.

pH of solution

8.8

7

* higher starting pH
* more immediate rise
* steep ascent near eq. point is not as long or as vertical
* eq. point is at center of rise but it's greater than 7

1/2 equivalence point

equivalence point

mL of strong base added to weak acid
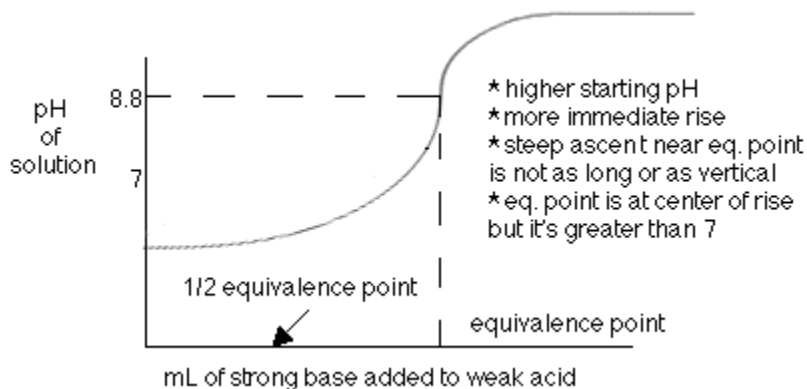
In an acid-base titration, the base will react with the weak acid and form a solution that contains the weak acid and its conjugate base until the acid is completely gone. To solve these types of

problems, we will use the weak acid's K_a value and the molarities in a similar way as we have before. Before demonstrating this way, let us first examine a short cut, called the **Henderson-Hasselbalch Equation**.
This can only be used when you have some acid and some conjugate base in your solution. If you only have acid, then you must do a pure K_a problem and if you only have base (like when the titration is complete) then you must do a K_b problem.

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

Where:
pH is the log of the molar concentration of the hydrogen
pKa is the equilibrium dissociation constant for an acid
[base] is the molar concentration of a basic solution
[acid] is the molar concentration of an acidic solution
Example Problem: 25.0 mL of .400 M KOH is added to 100. mL of .150 M benzoic acid, $HC_7H_5O_2$ (Ka=6.3×10^{-5}). Determine the pH of the solution.

Answer:
    Determine where in the titration we are :
        $0.400 \ M \times 0.025 \ L = 0.0100$ mol KOH added
        $0.150 \ M \times 0.100 \ L = 0.0150$ mol $HC_7H_5O_2$ originally
        because only 0.0100 mol of base has been added, that means the titration is not
        complete; this means there are two ways to solve this problem : the normal way
        and the way using the Henderson - Hasselbalch Equation.

    Normal Way:

	$HC_7H_5O_2$	+	OH⁻	→	$C_7H_5O_2^-$	+	H_2O
before reaction	0.0150 mol		0.0100 mol		0 mol		--
change	-0.0100		-0.0100		+0.0100		--
after reaction	0.0050		0		0.0100		--

$$Ka = \frac{[H^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = 6.3\times10^{-5} = \frac{(x)(0.0100)}{0.0050}$$

$$x = [H^+] = 3.2\times10^{-5} \ M$$

$$pH = -\log(3.2\times10^{-5}) = 4.49$$

    Henderson-Hasselbalch Way:

$$[HC_7H_5O_2] = \frac{0.0050 \text{ mol}}{0.125 \text{ L}} = 0.040 \ M$$

$$[C_7H_5O_2^-] = \frac{0.0100 \text{ mol}}{0.125 \text{ L}} = 0.0800 \ M$$

$$pH = pKa + \log\frac{[base]}{[acid]}$$

$$pH = -\log(6.3\times10^{-5}) + \log\frac{0.0800}{0.0400} = 4.20 + 0.30 = 4.50$$

 This equation is used frequently when trying to find the pH of buffer solutions. A buffer solution is one which resists changes in pH upon the addition of small amounts of an acid or a base. They are made up of a conjugate acid-base pair such as $HC_2H_3O_2/C_2H_3O_2^-$ or NH_4^+/NH_3. They work because the acidic species neutralize the OH^- ions while the basic species neutralize the H+ ions. The buffer capacity is the amount of acid or base the buffer can neutralize before the pH begins to change to an appropriate degree. This depends on the amount of acid or base in the buffer.

High buffering capacities come from solutions with high concentrations of the acid and the base and where these concentrations are similar in value.

Practice weak acid problem:
C_6H_5COONa is a salt of a weak acid C_6H_5COOH. A .10 M solution of C_6H_5COONa has a pH of 8.60.

1. calculate $[OH^-]$ of C_6H_5COONa
2. calculate K for: $C_6H_5COO^- + H_2O \longleftrightarrow C_6H_5COOH + OH^-$
3. calculate K_a for C_6H_5COOH

See the weak acid solution.

Practice titration problem:
20.00 mL of 0.160 M $HC_2H_3O_2$ ($K_a=1.8\times10^{-5}$) is titrated with .200 M NaOH.

1. What is the pH of the solution before the titration begins?
2. What is the pH after 8.00 mL of NaOH has been added?
3. What is the pH at the equivalence point?
4. What is the pH after 20.00 mL of NaOH has been added?

See the titration solution.

The Lewis Definition :
Lewis acidity
**5.7 Examples of Lewis acids and bases**
acid: accepts an electron pair
base: donates an electron pair
The advantage of this theory is that many more reactions can be considered acid-base reactions because they do not have to occur in solution.
5.11 The fundamental types of reaction
The Lewis Definition considers an acid to be an electron pair acceptor and a base as an electron pair donor. When they react, the resulting compound is called an *adduct* and the bond a *dative* bond. It encompasses the Brønsted/Lowry definition and many other reaction types:

$$H^+ \; + \; :OH^- \; \longrightarrow \; H_2O$$
$$F_3B \; + \; :NH_3 \; \longrightarrow \; F_3BNH_3$$
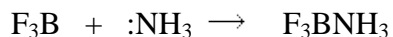
All the usual ligands can be viewed as Lewis bases and the metal ions as lewis acids.
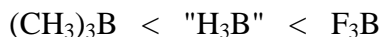**5.8 Boron and carbon group acids**
5.9 Nitrogen and oxygen group acids
5.10 Halogen acids

Acid/Base Strength and Electonic Effects

$$(CH_3)_3N: \; > \; H_3N: \; > \; F_3N:$$

$$(CH_3)_3B \quad < \quad "H_3B" \quad < \quad F_3B$$

In the above series, F is the most electron withdrawing and CH_3 the most electron releasing. However, there can be unexpected effects. Consider the observed order:

$$BF_3 \quad < \quad BCl_3 \quad < \quad BBr_3$$

The reduced strength of the fluoride compound is due to internal B-F π-bonding which goes some way towards satisfying the electron deficiency of the boron. A similar effect is observed in the $B(OR)_3$ compounds (relative to the S or Se analogues).

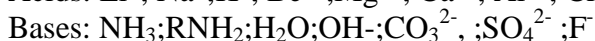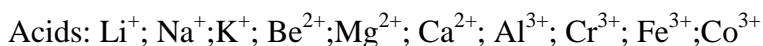**Systematics of Lewis acids and bases**

Towards protons, pyridine is a weaker base than 2-methyl or 4 methyl pyridine which are about equally stronger. However, towards $B(CH_3)_3$ the 4-methyl pyridine is the significantly stronger base. The methyl group of the 2-methyl pyridine gets in the way. A similar effect is seen with triethylamine and quinuclidine $(CH(CH_2CH_2)_3N$.

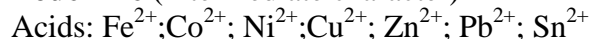Also, $B(CH_3)_3$ is a stronger acid than the highly hindered $B(C(CH_3)_3)_3$.

5.12 Hard and soft acids and bases
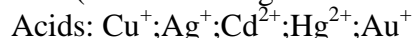
Hard and Soft Acids and Bases

Hard (Predominantly, having the electron concguration of inert gases)

Acids: Li^+; Na^+;K^+; Be^{2+};Mg^{2+}; Ca^{2+}; Al^{3+}; Cr^{3+}; Fe^{3+};Co^{3+}
Bases: NH_3;RNH_2;H_2O;$OH-$;CO_3^{2-}, ;SO_4^{2-} ;F^-

Boderline (Intermediate character)
Acids: Fe^{2+};Co^{2+}; Ni^{2+};Cu^{2+}; Zn^{2+}; Pb^{2+}; Sn^{2+}
Bases: Br^-; Cl^-
Soft (Electron confguration in the outer shell similar to Ni^o; Pb^o; Pt^o)
Acids: Cu^+;Ag^+;Cd^{2+};Hg^{2+};Au^+
Bases: CN^-;SCN^-;RSH;RS^-

Type (a) Hard Acids

- Alkali and alkaline earth metals
- Other lighter and highly charged cations e.g. Ti_4^+, Fe_3^+, Co_3^+, Al_3^+

Type (b) Soft Acids

- Heavier transition metal ions e.g. Hg_2^{2+}, Hg^{2+}, Pt^{2+}, Pt^{4+}
- Metals in lower oxidation states e.g. Ag^+, Cu^+ and zero metals

Hardness is associated with low polarizability and a tendency towards ionic bonding.

Softness is associated with greater polarizability and more covalent bonding.
The hard and soft characters are not absolute but gradually vary. HSAB RULES:
Thermodynamic equilibrium: Hard acids pre-
fer to associate with hard bases and soft acids with soft bases. Kinetics: Hard acids react readily with hard bases and
soft acids with soft bases. The basic principle is that like prefers like:

Complexes of Type (a) Metals	Ligands			Complexes of Type (b) Metals
Strongest bonding	R_3N	R_2O	F^-	Weakest bonding
	R_3P	R_2S	Cl-	
	R_3As	R_2Se	Br^-	
Weakest bonding	R_3Sb	R_2Te	I^-	Strongest bonding

5.13 Thermodynamic acidity parametersAcid/Base Strength and Steric Effects

The Drago-Wayland Equation

This empirical equation can be used to obtain a fairly quantitative value for ΔH_{ab}, the enthalpy of formation of and Lewis adduct:
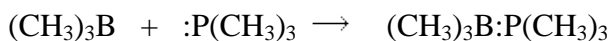
$-\Delta H_{AB} = E_A.E_B + C_A.C_B + W$

The factors E are a measure of the acid or base's tendency to form a bond by electrostatic interaction which is roughly correlated with hardness. Similarly the factors C go with the tendency to form a covalent bond, and is correlated with softness. Both factors are considered to be constant regardless of the partner. The factor W is almost always zero (always in the data given!) and is a fudge factor for use if it is suspected that and acid or a base makes a constant contribution to ΔH_{AB} which is not dependent on the partner and so should not be included in the product terms.

Table 7.2 lists the experimental E and C parameters for a variety of acids and bases. It must be understood that every adduct of a "new" acid or base whose ΔE_{AB} is measured allows a new entry to be added to the table. In the beginning four parameters, had to be given arbitarily assigned values (remember the Pauling electronegativity scale). They are marked [b]

As an example, consider:

$(CH_3)_3B + :N(CH_3)_3 \longrightarrow (CH_3)_3B:N(CH_3)_3$
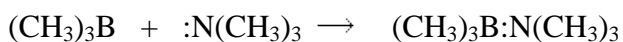
$-\Delta E = 5.79 \times 1.19 + 1.57 \times 11.20 = 24.47$ kcal mol^{-1}

$(CH_3)_3B + :P(CH_3)_3 \longrightarrow (CH_3)_3B:P(CH_3)_3$

$-\Delta E = 5.79 \times 1.11 + 1.57 \times 6.51 = 14.80$ kcal mol^{-1}

$"(CH_3)_3Al" + :N(CH_3)_3 \longrightarrow (CH_3)_3Al:N(CH_3)_3$
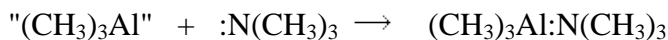
$-\Delta E = 17.32 \times 1.19 + 0.94 \times 11.20 = 31.14$ kcal mol^{-1}

$"(CH_3)_3Al" + :P(CH_3)_3 \longrightarrow (CH_3)_3Al:P(CH_3)_3$
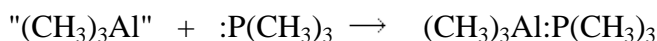
$-\Delta E = 17.32 \times 1.11 + 0.94 \times 6.51 = 25.35$ kcal mol^{-1}

The amine adducts are both stronger than the phosphine adducts, but the difference is much more marked for the harder boron. Unfortunately the table of acids does not contain any really soft

ones where the order of strength of the dative bond might be reversed.

5.2 Solvent leveling

Leveling Effect of Protonic Solvents

In any solution, the solvent is always the substance present in the largest amount. If the solvent contains ionizable protons it is said to be **protonic**, and if it is protonic, it will engage in acid-base reactions. Many solvents are protonic, including water, liquid ammonia, and glacial acetic acid. A protonic solvent is often amphiprotic, like water, and thus engages in acid-base reactio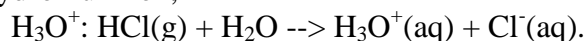ns. When an acid which is stronger than the conjugate acid of water, such as hydrochloric acid, is added to water the stronger acid will react with water to give the weaker acid which is the aquated proton or hydronium ion,

$$H_3O^+: HCl(g) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq).$$

All acids which are stronger than the hydronium ion will react with the essentially limitless supply of water to quantitatively produce hydronium ion, and so their strength will be leveled to that of the hydronium ion. This **levelling effect** is the reason why, in aqueous solution, the strongest acid which can exist is the hydronium ion. All others will be levelled to the hydronium ion by reaction. In aqueous solution hydrochloric acid, sulfuric acid, perchloric acid, and nitric acid are all equally strong.

As with acids, so also with bases. When a base which is stronger than the conjugate base of water, such as sodium oxide, is added to water the stronger base will react with water to give the weaker base which is the hydroxide ion,

$$OH^-: Na_2O(s) + H_2O \longrightarrow 2OH^-(aq) + 2Na^+(aq)$$
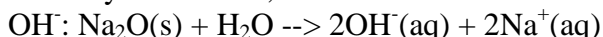
The actual base here is the oxide ion since the sodium ion is an extremely weak acid or base.

All bases which are stronger than the hydroxide ion will react with water to quantitatively produce hydroxide ion. Although oxide ion, amide ion, ethoxide ion, and methoxide ion are all stronger bases than is hydroxide ion, their strength in aqueous solution is leveled to that of hydroxide ion. Addition of sodium oxide rather than sodium hydroxide to water will not give a more basic solution. Sodium oxide, and the other oxides of alkali metals and alkaline earths, are called basic oxides because their aqueous solutions are basic. They are also referred to as anhydrides of hydroxides (from anhydrous, meaning "without water") because they act like hydroxides from which water has been removed.

The levelling effect operates in any protonic solvent. In liquid ammonia, for example, all acids are levelled to the strength of the ammonium ion, NH_4^+, and all bases are levelled to the strength of the amide ion, NH_2^-. Many of the acids which are weak in water act as strong acids in liquid ammonia because they are stronger than ammonium ion. On the other hand, not all of the bases which are strong in water are also strong in liquid ammonia.

Glacial acetic acid is another protonic solvent in which the levelling effect takes place. Glacial acetic acid can be used to show that hydrogen chloride is a weaker acid than is perchloric acid,

since hydrogen chloride behaves as a weak acid in glacial acetic acid. Methanol is also a protonic solvent in which some of the acids which are strong (completely dissociated) in water are found partially in molecular form.
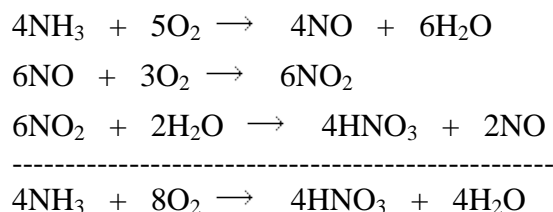
Periodic trends in Bronsted acidity
5.3 Periodic trends in aqua acid strength
## Sulphuric acid (H_2SO_4)

- One of the most important chemicals in industry. (About 40 megatons in 1981)
- Made from sulphur by burning it to SO_2 and then oxidizing the SO_2 to SO_3 by either the "lead chamber" process or the "contact" process. The older lead chamber process was a homogeneous catalytic cycle using oxides of nitrogen as the intermediate oxidizing agent. The concentration of sulphuric acid that could be produced was limited to 78%. The contact process uses a V_2O_3 heterogeneous catalyst. The process is sufficiently exothermic and the quantities are such that a sulphuric acid plant can be a source of industrial or domestic power.
- Concentrated sulphuric acid is 18 M or 98%. Pure sulphuric acid is made by adding the necessary amount of SO_3. Addition of excess SO_3 leads to "fuming suphuric acid" or "oleum" which contains polysulphuric acids.
- Sulphuric acid is a very effective (and dangerous) dehydrating agent: it can produce carbon from sugar $C_6H_{12}O_6$, for example. Never **ever** dilute concentrated sulphuric acid by adding water to it: always add the acid to water

Nitric Acid (HNO_3)

- Nitric acid is made by oxidizing ammonia with oxygen over heated Pt as catalyst:

$$4NH_3 \ + \ 5O_2 \ \longrightarrow \ \ 4NO \ + \ 6H_2O$$

$$6NO \ + \ 3O_2 \ \longrightarrow \ \ 6NO_2$$

$$6NO_2 \ + \ 2H_2O \ \longrightarrow \ \ 4HNO_3 \ + \ 2NO$$

$$\text{--}$$

$$4NH_3 \ + \ 8O_2 \ \longrightarrow \ \ 4HNO_3 \ + \ 4H_2O$$

- Concentrated nitric acid is about 70% by mass in water or 16 M.
- It is often slightly yellow due to th epresence of NO_2.
- There are autoionization equilibria in the pure colourless acid:

$$2HNO_3 \ \rightleftharpoons \ \ H_2NO_3^+ \ + \ NO_2^-$$

$$H_2NO_3^+ \ \rightleftharpoons \ \ NO_2^+ \ + \ H_2O$$
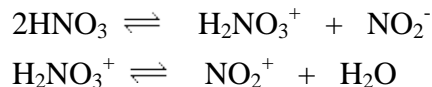
- The acid below 2 M is not very oxidizing, but the concentrated acid will dissolve almost all metals by its oxidizing action. Metals that are resistant are Au, Pt, Rh and Ir plus Al, Fe and Cu by oxide film passivation under certain conditions. The other product of oxidation to the metal ion is either NO or NO_2 depending on the acid concentration. Only Mg will produce H_2

Aqua Regia

This is a mixture of 3 volumes of concentrated hydrochloric acid to 1 volume of concentrated nitric acid. It contains free Cl_2 and ClNO and has very powerful oxidizing properties as well as being a strong acid. It is the acid of last resort to get metal into solution for analysis. It will dissolve Au and Pt which form $[AuCl_4]^-$ and $[PtCl_6]^{2-}$. Mercuric sulphide will dissolve because the sulphide is oxidized to SO_2 and the mercuric ion is in the form of $[HgCl_4]^{2-}$

Perchloric Acid

- Normally comes as a 70 - 72% solution in water.
- Pure perchloric acid is made by dehydrating the aqueous solution over $Mg(ClO_4)_2$. It is not vey stable and decomposes to the anhydride, Cl_2O_7.
- The aqueous acid and the pure compound both react explosively with organic materials and certain inorganic compounds. Exercise extreme caution.
- *Pure* perchloric acid is a "superacid" with $H_o = -13.8$.

Hydrohalic Acids (except HF)

- They are similar to oneanother except HF is anomalous.
- They are all gases as pure substances which are very soluble in water in which they are 100% dissociated.
- *Pure* HCl (b.p. -85 ^{o}C) autoionizes to a small extent like HF:

$$3HCl \; \rightleftharpoons \; H_2Cl^+ \; + \; HCl_2$$
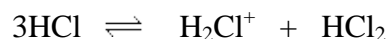
Compounds of both ions have been isolated too.

Because Br- and I- are reducing agents, the acids do not always give the simple products expected in an acid/base reaction.

Hydrofluoric Acid

- In aqueous solution, it is a weak acid, $K = 7.2 \times 10^{-5}$

because the H_3O^+ ion is stabilized by H-bonding to the F^- ions.

- Hydrofluoric acid is difficult to work with because is attacks glass and silica giving gaseous SiF_4 or the $[SiF_6]^{2-}$. It also causes burns which are very slow to heal or even get progressively worse. Exercise extreme caution.
- Pure HF is a very strong acid and autoionizes:

$$2HF \; \rightleftharpoons \; H_2F^+ \; + \; F^-$$
$$F^- \; + \; nHF \; \rightleftharpoons \; HF_2^-, H_2F_3^-, H_3F_4^-, ...$$

- Very few compounds exist which are strong enough F^- acceptors to be considered acids. An example is SbF_5 which leads to pure HF having superacid properties.

- Pure HF has a dielectric constant $\varepsilon/\varepsilon_o = 84$ and is a good solvent like water which is surprisingly gentle. It can be used for example to remove Fe from metalloproteins without damaging the apo-protein primary structure.
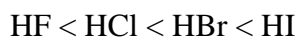
Binary Acids:

Compounds containing acidic protons bonded to a more electronegative atom.

e.g. HF, HCl, HBr, HI, H_2S

The acidity of the haloacid (HX; X = Cl, Br, I, F)

Series increase in the following order:

$HF < HCl < HBr < HI$

5.4 Simple oxoacids

Compounds containing acidic - OH groups in the molecule.
Acidity of H_2SO_4 is greater than H_2SO_3 because of the extra O (oxygens) attached to S pulling electrons away making H^+ to come off easier.

The order of acidity of oxyacids with a halogen (Cl, Br, or I) shows a similar trend.

$HClO_4$	$HClO_3$	$HClO_2$	$HClO$
Perchloric	chloric	chlorus	hyphochlorus

The Strengths of the Oxyacids

Consider compounds of type: $XO_n(OH)_m$ e.g. $PO(OH)_3$ $Te(OH)_6P$

- The successive K's differ by 10^{-4} to 10^{-5} or $pK_{n-1} - pK_n = 4.5 \pm 0.5$.
- The magnitude of K_1 depends on the number of X=O groups:

Number of X=O's	K_1	Acid Strength
3	very very large	very strong

2	$\sim 10^2$	strong
1	$\sim 10^{-2}$ - 10^{-3}	medium
0	$\sim 10^{-7.5}$ - $10^{-9.5}$	weak

    a. The more X=O groups there are, the more canonical structures are available to delocalize the charge and stabilize the anion. Perchloric acid is very acidic and telluric acid is weak.

    b. Exceptions have a deceiving formula, for example, phosphorous acid, H_3PO_3 is really $HPO(OH)_2$ and H_3PO_2 is really $H_2PO(OH)$ where only the OH protons are ionizable, but the acids are stronger than one might guess ($K_1 = \sim 10^{-2}$ for both). An the other hand, carbonic acid, $(HO)_2CO$ ($K_1 = 2 \times 10^{-4}$) is really largely dissociated to a solution of CO_2 in water and is weak by dilution, rather than inherently. Its apparent K_1 is $\sim 10^{-6}$

5.6 Polyoxo compound information

Polyoxoanions of general composition $[X_aM_bO_c]^{d-}$ (X= P, Si; M =W, Mo) have applications in various disciplines including medicine, catalysis, and separations science. In prospective applications relating to nuclear waste remediation and processing, they generally function as complexants to sequester and stabilize f ions, R. Remarkably, there is a dearth of fundamental information about the redox behavior and coordination of 4f (lanthanide) and 5f (actinide) ions in polyoxoanion clusters with different X-M-O framework structures. The interest with polyoxoanions concerns their interactions with multivalent f elements. Two polyoxoanion systems—[P5W30O110]15- and [P2W17O61]10-—have attracted our attention because of their remarkable electrochemistry. Both are oxidants: multielectron reduction of the P-W-O frameworks is reversible and nondestructive. By using synthetic methods, spectroscopic, and electrochemical techniques, we are obtaining insights
that are leading to a predictive understanding of the mechanisms by which the polyoxoanions and f ions are each affected by their mutual complexation.
Polyoxometalates constitute model systems for the study of the electron and energy transfer in the infinite metaloxide
lattice and their simplicity allows to treat at the molecular scale the coupling of electronic and nuclear movements, which is an inherent problem for the mixed-valence systems. As is clear from such a variety of both structure and reactivity of polyoxometalates, current research on polyoxometalates are
1) structure/reactivity relationships with particular regard to the mechanism of electron transfer reactions, 2) magnetic interaction and molecular magnetic device, 3) energy-transfer mechanism and luminescence device (including nonlinear optical
device), 4) encapsulation of templates in the photo-induced self-assembly process, 5) template-exchange reaction
and topology, and 6) antibacterial effects on MRSA and VRE.

5.14 Solvents as acids and bases

Solvent Properties
Their usefulness is a function of:

1. Liquid temperature range
2. Dielectric constant
3. Its Lewis acid/base properties
4. Its Brønsted/Lowry acid base properties
5. Autodissociations properties

Liquid Range
The most useful are liquid at room temperature but we often need solvents to go upto high or low temperatures. The range is large for DMF and propane-1,2-diol carbonate. Ammonia is a good solvent for many reactions but it boils at about -33°C. Hydrogen fluoride, which boils at about 20 ^{o}C is also useful, but very corrosive.
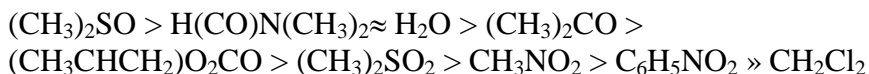
Dielectric Constant

This factor is important if the sovent is to dissolve ionic compounds. Water happens to have a very high dielectric constant (82) and is probably the best all-round solvent for ionic compounds that we have. The key formula here is:

$$F = q^+q^-/4\pi\epsilon r^2$$

Lewis Acid/Base Properties

The extent to which the sovent can act as a ligand towards the ions of an ionic solute, with the dielectric constant which is related but not directly, determines how good a solvent it will be. In the crystal lattice with simple ions, the anions effectively complex the cations and vice versa. The solvent will have to do a better job.

Generally, because the cations are smaller than the anions, the greatest gains are to be made by effective complexation of the cations, so it is the Lewis basicity of the solvent that is more important. For common solvents:

$(CH_3)_2SO > H(CO)N(CH_3)_2 \approx H_2O > (CH_3)_2CO >$
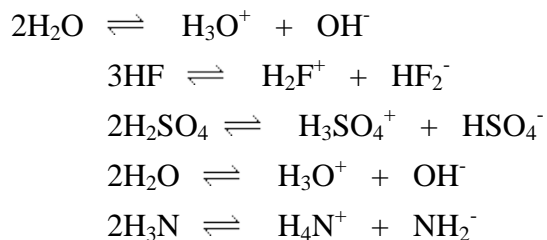$(CH_3CHCH_2)O_2CO > (CH_3)_2SO_2 > CH_3NO_2 > C_6H_5NO_2 \gg CH_2Cl_2$
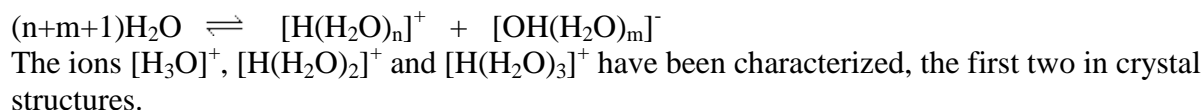
Protic Solvents

These solvents contain protons which can be inozed, in other words the solvent is a Brønsted acid. Examples are H_2O, HF, H_2SO_4, HCN and even MH_3.

Autodissociation

Also known as autoionization, so examples in protic solvents are:

$$2H_2O \;\rightleftharpoons\; H_3O^+ + OH^-$$
$$3HF \;\rightleftharpoons\; H_2F^+ + HF_2^-$$
$$2H_2SO_4 \;\rightleftharpoons\; H_3SO_4^+ + HSO_4^-$$
$$2H_2O \;\rightleftharpoons\; H_3O^+ + OH^-$$
$$2H_3N \;\rightleftharpoons\; H_4N^+ + NH_2^-$$

The cations and anions produced can interact with the solutes helping to explain certain reaction products. Also, the autodissociation reactions are not really this simple - consider water: The more general equation is:

$$(n+m+1)H_2O \;\rightleftharpoons\; [H(H_2O)_n]^+ + [OH(H_2O)_m]^-$$

The ions $[H_3O]^+$, $[H(H_2O)_2]^+$ and $[H(H_2O)_3]^+$ have been characterized, the first two in crystal structures.

$K'_{25\,^{o}C} = [H^+][OH^-]/[H_2O] = (1.0 \times 10^{-14})/55.56$ and $K_{25\,^{o}C} = [H^+][OH^-] = 1.0 \times 10^{-14}$
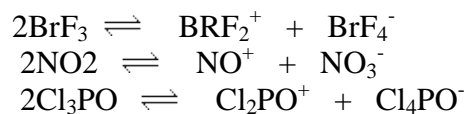
Aprotic Solvents

Such solvents fall into three broad classes:

1. Non-polar, or weakly polar solvents which do not dissociate and are not strongly coordinating. Examples are hydrocarbons and CCl_4. They are poor solvents for everything except like substances, i.e. other nonpolar molecules.
2. Strongly solvating (usually polar) solvents which do not dissociate. Examples are acetonitrile (CH_3CN), N,N-dimethyformamide (DMF, $H(CO)N(CH_3)_2$), dimethyl sulphoxide (DMSO ($CH_3)_2SO$), tetrahydrofuran (THF C_4H_8O) and liquid sulphur dioxide (SO_2).

   They are similar in being very strongly coordinating towards cations although SO_2 forms an adduct with acetonitrile. The dielectric constants can very quite a bit (DMSO = 45, THF = 7.6) which will govern their ability to dissolve ionic materialas.

3. Highly polar and autoionizing solvents. Examples are:

$$2BrF_3 \;\rightleftharpoons\; BRF_2^+ + BrF_4^-$$
$$2NO2 \;\rightleftharpoons\; NO^+ + NO_3^-$$
$$2Cl_3PO \;\rightleftharpoons\; Cl_2PO^+ + Cl_4PO^-$$

Molten Salts

These are the extreme case of autoionizing solvents. Generally they will be very high temperature systems but lower temperatures can be attained by the right eutectic mixtures, e.g.

LiNO$_3$/NaNO$_2$/KNO$_3$ mixtures can reach as low as 130 ^{o}C
(C$_2$H$_5$)$_2$NH$_2$Cl melts at 215 ^{o}C
[N,N-RR'N$_2$C$_3$H$_3$]$^+$Cl$^-$ with AlCl$_3$ can be liquid at room temperature.
Uses:
Aluminum is made by electrolyis of Al$_2$O$_3$ in a cryolite {Na$_3$AlF6]
Re$_3$Cl$_9$ + Et$_2$NH$_2$Cl $\rightleftharpoons$ [Et$_2$NH^2][Re$_2$Cl$_8$] with its quadruple bond.

Solvents for Electrochemistry
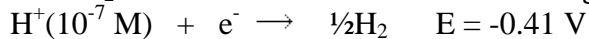
Solvent which are useful for electrochemistry must have two characteristics: a highish
dielectric constant so that they are good solvents for ionic compounds, and they must be
redox resistant. Water is actually not ideal because, although its dielectric constant is very
high, it is susceptible to both oxidation and reduction at relatively small potentials:
H$_2$O $\longrightarrow$ O$_2$ + 4H$^+$(10^{-7} M) + 4e$^-$ E = -0.82 V
i.e. ½X$_2$ + e- $\longrightarrow$ X$^-$ E > +0.82 V might generate oxygen from water
H$^+$(10^{-7} M) + e$^-$ $\longrightarrow$ ½H$_2$ E = -0.41 V
i.e. M $\longrightarrow$ M$^+$ + e$^-$ E > +0.41 V might generate H$_2$ from water
Acetonitrile or DMF are often used as an electrochemistry solvent for example in cyclic
voltammetry for organometallic substances usually with a redox inert supporting
electrolyte such as t-butylammonium perchlorate.
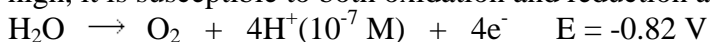
Purity of Solvents

Water and oxygen are th most common contaminants and they can be very difficult to
remove. Many research labs have several continuously operating stills from which the
solvents can be removed under cover of nitrogen or argon. Hydrocarbon solvents and
ethers can be distilled over sodium (or potassium) in the presence of benzoquinone as an
intense blue indicator (of dryness). Various hydrides can also be used.

More reactive solvents can be dried effectively over molcular sieves and vacuum
distilled to remove dissolved oxygen.

It is important to remember that even traces of contaminents will mess up sensitive
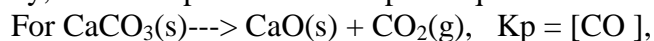reactions because the solvent is present in such excess.

Heterogeneous acid-base reactions
Heterogeneous equilibria.
Heterogeneous equilibria have more than one phase present in the reaction. We have discussed
how to write equilibria expressions for solutions (use K) and gases (use K). What about:
                    CaCO$_3$(s)---> CaO(s) + CO$_2$(g)
Recall that in equilibria expressons, [A] actually means the ratio of the concentration in M to the
concentration of the standard state. The standard state concentrations are (a) that of the pure
solid, (b) that of a pure liquid. Hence, [A] for a pure solid or a pure liquid is 1 by definition.
Consequently, terms for pure solids and pure liquids do NOT appear in equilibria expressions.
        For CaCO$_3$(s)---> CaO(s) + CO$_2$(g),   Kp = [CO],
Acid-base catalysis is of great importance in large scale chemicals processing, e.g. petroleum

refining. Mineral acids are often used in these industrial processes; however, these liquids are corrosive, dangerous, and difficult to dispose of. Efforts have been made to replace liquid acids with solid catalysts such as acidic resins, supported Lewis-acids, zeolites, phosphates, and modified metal oxide based systems; demanding that the acidity of these materials be characterized. The numerous concepts which have been developed to describe acidity (e.g. Brønsted, Lewis, Pearson, Arrhenius, Bjerrum), very often for selected materials/systems, reflect the difficulty in finding a general approach to the subject and a widely applicable technique of measurement. Measurements of acidity are usually indirect, i.e. they evaluate the interaction of an acid with a "probe". The pH scale is a precise definition and measure of Brønsted acidity but it is actually a very specific case: the interaction of a proton donor type acid with the probe molecule water in the solvent water. The equilibrium acid/probe is influenced by the proton donor capability of the acid, the proton acceptor capability of the probe, and the solvation of all species involved.

Transferring these ideas to solid surfaces with Brønsted sites it becomes evident that again proton donor and acceptor
capabilities of acid site and probe molecule are important but also the coordination of the probe molecule – particularly a large
molecule – to atoms surrounding the proton, thus the geometry of the entire "site". With this background, it becomes
understandable that acidity scales of solid surfaces can successfully be established when a "family" of samples is investigated,
i.e. structurally related compounds (e.g. zeolites with different Si/Al ratios), while comparing results from different probes or
different materials often reveals inconsistencies. This also explains why acidity measurements may not help to predict reactivity,
i.e. if the reactant and the probe are chemically non related. Understanding the reaction mechanism and the role of acid sites in
the initiation or the propagation of a reaction, often a chain reaction in acid catalysis, is essential to allow a correlation of
acid-base-properties and reactivity.

Super Acids

A superacid is defined as any acid stronger than 100% sulfuric acid. In organic chemistry, superacids have been used extensively to stabilize carbocations (R_3C^+, protonated arenes, etc.). These cations are typically characterized by NMR spectroscopy at low temperatures. In inorganic chemistry, superacids have been used to observe a wide variety of reactive cations (S_8^{2+}, $H_3O_2^+$, Xe_2^+, HCO^+, etc.), some of which have been isolated for structural characterization. Nevertheless, many compounds decompose in typical superacid media and desired reactive cations cannot be observed (e.g. R_3Si^+, C_{60}^+, HC_{60}^+, P_4^+ etc.). This identifies two of the major limitations of presently known superacids: the nucleophilicity of their anions and the oxidizing power of the added Lewis acid. For example, the silylium ion (R_3Si^+) cannot be closely approached in a typical superacid such as HF/SbF_5 because F^- and SbF_6^- anions coordinate to silicon. C_{60}^+ is unstable in HF/SbF_5 because of oxidative destruction. Even the supposedly non-oxidizing triflic acid, CF_3SO_3H, is reported to decompose C_{60}. In addition,

superacids are typically viscous, corrosive liquids -- difficult to handle stoichiometrically and limited in their commercial applications.

The strongest acid in aqueous solution is H_3O+ since all the strong acids protonate water to 100% of their capacity. In non-aqueous solution it is possible to generate more powerful proton donors.

The strength of such strong acids is measured by the Hammett acidity function:

$$H_o = pK_{BH}{}^+ - \log([BH^+]/[B])$$

Here B and BH^+ usually refer to a colorimetric indicator, that is either B or (more likely) BH^+ is strongly coloured, and $pK_{AB}{}^+$ is small or negative. Typical indicators are:

Indicator	$pK_{AB}{}^+$ (in H_2SO_4)
m-nitroaniline	+2.5*
p-nitroaniline	+0.99*
o-nitroaniline	-0.29
2,4-dinitroaniline	-4.53
3-methyl-2,4,6-trinitroaniline	-8.22
2,4,6-trinitroaniline	-10.10

*The first two provide overlap with the normal range of the pH scale (~0 - 14).

Notice that the Hammett scale is actually equivalent to the pH scale in the case of aqueous solutions:

A table of selected H_o values is given below. In each case, the equilibrium leading to the proton donor species is shown.

$$H_o = -\log([B][H^+]/[BH^+] - \log([BH^+]/[B]) = -\log[H^+]$$

Acid	H_o
$2H_2SO_4 \rightleftharpoons H_3SO_4{}^+ + HSO_4{}^-$	-12
$H_2SO_4 + H_2S_2O_7 \rightleftharpoons H_3SO_4{}^+ + HS_2O_7{}^-$ (in oleum)	-15
$3HF \rightleftharpoons H_2F^+ + HF_2{}^-$	-11
$2HF + SbF_5 \rightleftharpoons H_2F^+ + HSBF_6$	-12
$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^-$	-15
$2HSO_3F + SbF_5 \rightleftharpoons H_2SO3F^+ + SbF_5SO_3F^-$	-19

The super acids can be used in a variety of reactions leading to unusual cations:

$$(CH_3)_3COH \; + \; \text{super acids} \; \longrightarrow \; (CH_3)_3C^+ \; + \; H_2O$$

$$I_2 \; + \; \text{super acids} \; \longrightarrow \; I_2^+ \text{ or } I_3^+$$