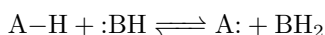


## Topic IV

# Hard-Soft Acid-Base and Donor-Acceptor Concepts of Transition Metals

### IV.1 Module 24: Acid-Base Chemistry

- 2/8: • Brønsted-Lowry Acid-Base Theory of Acids and Bases (1923).
- Acid: Any chemical species (molecule or ion) that is able to lose, or “donate,” a hydrogen ion (proton).
  - Base: Any chemical species that is able to gain, or “accept”, a proton.
    - A base must have a pair of electrons available to share with the proton; this is usually present as an unshared pair, but sometimes is in a  $\pi$  orbital.
  - Acid-base reactions: The transfer of a proton from an acid to a base.



- Protons do not exist free in solution but must be attached to an electron pair.
- Water is amphoteric.
- In the Brønsted-Lowry paradigm, we cannot separate the acids/bases from the solvent (no protons; only *solvated* protons). In a non-aqueous medium such as DMSO, however, we have much broader scope of acids and bases.
- **Carbon acid:** Any molecule containing a C–H bond can lose a proton forming the carbanion.
- Carborane ( $\text{H}(\text{CHB}_{10}\text{Cl}_{11})$ ) is a superacid one million times stronger than sulfuric acid since its conjugate basis is incredibly stable (super easy to delocalize the charge).
- The base dissociation constant or  $K_b$  is a measure of basicity.  $\text{p}K_b$  is the negative log of  $K_b$  and related to the  $\text{p}K_a$  by the simple relationship  $\text{p}K_a + \text{p}K_b = 14$ . The larger the  $\text{p}K_b$ , the more basic the compound.
- **Superacid:** An acid with acidity greater than that of 100% pure sulfuric acid.
  - In water, the strongest acid you can have is  $\text{H}_3\text{O}^+$ .
  - The strongest superacids are prepared by the combination of two components, a strong Lewis acid and a strong Brønsted-Lowry acid.
  - Fluoroantimonic acid  $\text{HF-SbF}_5$  is  $2 \times 10^{19}$  stronger than 100% sulfuric acid.

- Olah's magic acid ( $\text{FSO}_3\text{H}-\text{SbF}_5$ ) can dissolve paraffin (candle wax; extremely inert), converting methane into the t-butyl carbocation.
- **Hammett acidity function:** Can replace the pH in concentrated solutions. *Also known as  $H_0$ .*
$$H_0 = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]}$$
  - Let  $\text{BH}^+$  be the conjugate acid of a very weak base B, with a very negative  $\text{p}K_{\text{BH}^+}$ . In this way, it is rather as if the pH scale has been extended to very negative values.
  - Hammett originally used a series of anilines with EWGs for the bases.
- **Superbase:** A compound that has a high affinity for protons.
  - Again, these do not exist in water.
  - Often destroyed by water,  $\text{CO}_2$ , and  $\text{O}_2$ .
  - A superbase has been defined as an organic compound whose basicity is greater than that of proton sponge, which has conjugate  $\text{p}K_{\text{a}}$  of 12.1.
  - These are valuable in organic chemistry, which abounds in very weak acids.
  - A common superbase is lithium diisopropylamide.

## IV.2 Module 25: Acid-Base Chemistry: Lewis Acids and Bases

2/10:

- The second midterm will be Saturday, February 20.
- Talapin will hold office hours this Friday from 3:00-4:00 PM.
- **Lewis acid:** Any species with a vacant orbital.
  - An atomic or molecular species that has an empty atomic or molecular orbital of low energy (LUMO) that can accommodate a pair of electrons.
- **Lewis base:** A compound with an available pair of electrons, either unshared or in a  $\pi$  orbital.
  - An atomic or molecular species that has a lone pair of electrons in the HOMO.
- Examples of Lewis acids:
  - The proton, onium ions (e.g.,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ), metal cations (e.g.,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ), trigonal planar species (e.g.,  $\text{BF}_3$ ,  $\text{CH}_3^+$ ), and electron-poor  $\pi$ -systems (e.g., enones, tetracyanoethylene [TCNE]).
- **Lewis base adduct:** The product of a Lewis acid reaction.
  - Simple Lewis acids:
    - Examples include  $\text{BF}_4^-$  in  $\text{BF}_3 + \text{F}^- \longrightarrow \text{BF}_4^-$  and  $\text{BF}_3\text{OMe}_2$  in  $\text{BF}_3 + \text{OMe}_2 \longrightarrow \text{BF}_3\text{OMe}_2$ , which are Lewis base adducts of  $\text{BF}_3$ .
    - In many cases, Lewis base adducts violate the octet rule.
    - In some cases, Lewis acids can bind to two Lewis bases (e.g.,  $\text{SiF}_4 + 2\text{F}^- \longrightarrow \text{SiF}_6^{2-}$ ).
  - Complex Lewis acids:
    - Most compounds considered to be Lewis acids require an activation step prior to the formation of the adduct.
    - For example, the reaction  $\text{B}_2\text{H}_6 + 2\text{H}^- \longrightarrow 2\text{BH}_4^-$  goes through the intermediate  $\text{B}_2\text{H}_7^-$ .
- The proton ( $\text{H}^+$ ) is one of the strongest but is also one of the most complicated Lewis acids. It is convention to ignore the fact that a proton is heavily solvated (bound to solvent). With this simplification in mind, acid-base reactions can be viewed as the formation of adducts.

- For example,  $\text{H}^+ + \text{NH}_3 \longrightarrow \text{NH}_4^+$  and  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$ .
- In the first reaction, essentially what happens is the frontier orbitals of  $\text{H}^+$  and  $\text{NH}_3$  are very similar in energy, and thus strongly combine when they form bonding and antibonding orbitals. Two electrons previously in the HOMO of  $\text{NH}_3$  drop the bonding energy into the new lower MO of  $\text{NH}_4^+$ . More rigorously, we have to account for the change in symmetry group from  $C_{3v}$  to  $T_d$ , but the above description basically encapsulates what happens.
- Examples of Lewis bases:
  - $\text{NH}_{3-x}\text{R}_x$  where  $\text{R}$  = alkyl or aryl.
  - $\text{PR}_{3-x}\text{A}_x$  where  $\text{R}$  = alkyl and  $\text{A}$  = aryl.
  - Compounds of O, S, Se, and Te in oxidation state 2, including water, ethers, and ketones.
  - Simple anions (e.g.,  $\text{H}^-$ ,  $\text{F}^-$ ), other lone pair-containing species (e.g.,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$ ,  $\text{CH}_3^-$ ), complex anions (e.g., sulfate), and electron-rich  $\pi$ -systems (e.g., ethyne, ethene, benzene).
- To quantify the strength of Lewis acids and bases, compare the standard enthalpies of complexation in kJ/mol.
  - For example, heats of binding of Lewis bases to  $\text{BF}_3$ .
  - We do this because we cannot use  $\text{p}K_b$  in the same way as we can in the Brønsted-Lowry description.
- **Electrides:** Compounds where the anions are electrons.
  - Put an alkali metal in liquid ammonia; the deep blue color comes from solvated electrons floating freely in solution surrounded by ammonia molecules.
  - If you add a very strong complexing agent for alkali metal ions to the solution, then the electrons will not be able to react back with the alkali metal and we will have crystallized an electride.
  - Electrides are dielectrics.
- The power of the Lewis approach is that it allows us to classify many reactions as acid-base reactions.
  - For example, Wilkinson's catalyst ( $\text{Rh}(\text{PPh}_3)\text{Cl}$  where  $\text{Ph}$  is a phenyl group) is probably the first hydrogenation catalyst to be explained.
  - The Lewis approach allows us to view every step in the mechanism<sup>[1]</sup> as an acid-base reaction.

### IV.3 Module 26: Hard and Soft Acids and Bases (HSAB) Principle

- HSAB principle can't be derived, but it's been proven to be a very powerful tool for chemists.
- The affinity of hard acids and hard bases for each other is mainly ionic in nature, whereas the affinity of soft acids and bases for each other is mainly covalent in nature.
- Hard acids and hard bases tend to have:
  - Small atomic/ionic radius.
  - High oxidation state.
  - Low polarizability.
  - High electronegativity.
  - Energy low-lying HOMO (bases) or energy high-lying LUMO (acids).

---

<sup>1</sup>We will study this mechanism in depth in CHEM 20200.

- Examples:  $\text{H}^+$ , alkali ions,  $\text{OH}^-$ ,  $\text{F}^-$ .
- Small stabilization energy when bonding, so attraction is mostly electrostatic.
- Soft acids and soft bases tend to have:
  - Large atomic/ionic radius.
  - Low or zero oxidation state.
  - High polarizability.
  - Low electronegativity.
  - Energy high-lying HOMO (bases) or energy low-lying LUMO (acids).
  - Examples:  $\text{CCH}_3\text{Hg}^+$ ,  $\text{Pt}^{2+}$ ,  $\text{H}^-$ ,  $\text{R}_3\text{P}$ ,  $\text{I}^-$ .
  - Large stabilization energy when bonding, so attraction is mostly covalent.
- Hard acids don't readily react with soft bases and vice versa.
- You should be able to intuitively classify acids/bases as hard or soft.

1 H																	<div><div></div><div></div><div></div></div> <div>hard    soft    intermediate</div>		
3 Li	4 Be																		
11 Na	12 Mg													13 Al	14 Si				
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As					
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Te	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb					
55 Cs	56 Ba			72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi				
87 Fr	88 Ra																		

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------

89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk
----------	----------	----------	---------	----------	----------	----------	----------	----------

Figure IV.1: Hard vs. soft metal ions.

- The affinity that metal ions have for ligands is controlled by size, charge, and electronegativity.
- This can be refined further by noting that for some metal ions, their chemistry is dominated by size and charge, while for others it is dominated by their electronegativity. These two categories of metal ions have been termed by Pearson as **hard** (metal ions) and **soft** (metal ions).
- Soft Lewis acids are transition metals with unusually high electronegativities (these go against typical periodic trends).
  - Note that QMech can't explain this island of high electronegativities in the transition metals; we need relativistic corrections and Dirac equations.

- The higher electronegativity stabilizes the LUMO of the acid.
- These ions are a treasure trove for catalytic chemistry.
- **Chemical hardness:** One half the difference between the ionization potential  $I$  and the electron affinity  $A$ .

$$\eta = \frac{I - A}{2}$$

- Note that the above equation cannot be applied to anions because electron affinity cannot be measured for them; the assumption is made that  $\eta$  for an anion  $X^-$  is same as that for the radical  $X^\bullet$ .
- Related to the **Mulliken electronegativity**:

$$\chi = \frac{I + A}{2}$$

- **HSAB principle:**

- (i) Hard acids prefer to bond to hard bases, and soft acids prefer to bond to soft bases.
  - Note that this rule has nothing to do with acid or base strength but merely says that the product  $A-B$  will have extra stability if  $A$  and  $B$  are both hard or both soft.
- (ii) A soft Lewis acid and a soft Lewis base tend to form a covalent bond, while a hard acid and a hard base tend to form ionic bonds.

- **Solubility:** Hard solvents (e.g., HF, H<sub>2</sub>O, and the protic solvents) tend to solvate strong solute bases (e.g., F<sup>−</sup> and the oxygen anions). Dipolar aprotic solvents (e.g., Me<sub>2</sub>SO and CH<sub>3</sub>COCH<sub>3</sub>) are soft solvents with a preference for solvating large anions and soft bases.

- For example,  $LiI + AgF \longrightarrow LiF + AgI$ . In this reaction, two mixed reactants recombine exothermically to form a hard-hard product and a soft-soft precipitate. Because of the Lewis definition, we can treat this as an acid-base reaction.

Classification		Hard	Intermediate	Soft	
		F <sup>−</sup>	Cl <sup>−</sup>	Br <sup>−</sup>	I <sup>−</sup>
Soft	Ag <sup>+</sup>	0.4	3.3	4.7	6.6
Intermediate	Pb <sup>2+</sup>	1.3	0.9	1.1	1.3
Hard	Fe <sup>3+</sup>	6.0	1.4	0.5	-

Table IV.1: Hard and soft formation constants.

- As another example, we can see in Table IV.1 that soft-soft and hard-hard ions have higher formation constants ( $\log K_1$ ) than any other combination, and hard-soft ions have lower formation constants than any other combination.
- **Coordination chemistry:** Numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.
- Au (I) is the softest metal ion.
  - Soft to the extent that compounds such as AuF and Au<sub>2</sub>O are unknown.
  - Nevertheless, it forms stable compounds with soft ligands such as cyanide.
- Al (III) is a very hard metal ion.
  - It has very high formation constants with both F<sup>−</sup> and OH<sup>−</sup>; additionally, it has virtually no affinity in solution for heavier halides such as Cl<sup>−</sup>.

- Its solution chemistry is dominated by its affinity for  $F^-$  and for ligands with negative O-donors.
- **Symbiosis effect:** Taking a borderline element and reacting it with a soft Lewis base to soften it, or a hard Lewis base to harden it.
  - For example,  $B^{3+}$  can be reacted with  $3H^-$ , we make the soft compound  $BH_3$ . If we react it with  $3F^-$ , we make the hard compound  $3BF_3$ .
  - Now  $BH_3$  and  $F^-$  do not react, but we can further soften it in the reaction  $BH_3 + H^- \longrightarrow BH_4^-$ .
  - Similarly,  $BF_3$  and  $H^-$  don't react, but we can further harden  $BF_3$  by reacting it with  $F^-$  to form  $BF_4^-$ .
- There is a preference against combining hard and soft ligands in the first coordination sphere. Examples:
  - $CH_3F + CF_3I \rightleftharpoons CH_3I + CF_4$  since  $CH_3^+$  and  $I^-$  are soft while  $CF_3^+$  and  $F^-$  are hard.
  - $Co(NH_3)_5F$  is stable since it has all hard ligands, but  $Co(NH_3)_5I$  will react with  $H_2O$  to produce  $Co(NH_3)_5OH$  since the former combines hard and soft and the latter does not.
  - Thiocyanate is **ambidentate**. Thus, we have Fe–N bonds in  $Fe(NCS)_6^{3+}$  (with the hard Fe (III) ion) and Au–S bonds in  $Au(SCN)_2^-$  (with the soft Au (I) ion).
    - Note that intermediate metal ions tend to bond to thiocyanate through nitrogen; indeed, intermediate Cu (II) forms  $Cu(NCS)_4^{2-}$ .
- **Ambidentate** (ligand): A polyatomic ligand that can bind through more than one of its constituent atoms.

## IV.4 Module 27: Steric Effects in Inorganic Chemistry

2/12:

- Chemistry is a game of two players: Electronic and steric effects.
- Gallanes, gallenes, cyclogallenes, and gallynes:
  - Various compounds with gallium.
  - React gallium (III) chloride with a Grignard reagent containing mesityl (2,4,6-trimethylphenyl; Mes;  $Me_3C_6H_2$ ):  $3(Me_3C_6H_2)MgBr + GaCl_3 \xrightarrow{-3MgBrCl} Ga(Me_3C_6H_2)_3$ .
  - A molecule with even more steric hindrance: a three gallium ring with a 2,6-dimesitylphenyl groups attached to each gallium.
  - The triphenylcyclopropenium cation is aromatic but the cyclogallene dianion is metalloaromatic.
  - In another compound, a  $Ga \equiv Ga$  triple bond holds two massive groups together.
    - The debate over this is a good example of chemistry not being black and white.
  - Acetylene and gallyne both show band structure.
    - Additionally, the former is linear while the latter is trans-bent with a donor-acceptor bond lacking a sigma bond.
    - To learn more about such bonding, read Power (2010).
- Steric effects are much more common in Lewis acid-base reactions in which larger acids are used.
  - With a small acid, increasing size in the base (i.e., replacing hydrogens with methyl groups) correlates with increasing strength.
  - With a large acid, decreasing size in the base correlates with increasing strength.
- Frustrated Lewis pairs:
  - Excessive steric bulk can prevent acids and bases from reacting to form an adduct.

- However, you can also have alternate reactions that yield compounds with Lewis acidic *and* Lewis basic regions.
- Frustrated Lewis pairs can activate (cleave)  $\text{H}_2$ .
  - They can also activate  $\text{CO}_2$ ; this has applications in the realm of  $\text{CO}_2$  sequestration.

## IV.5 Chapter 6: Acid-Base and Donor-Acceptor Chemistry

From Miessler et al. (2014).

- IUPAC calls hydronium “oxonium” and uses “hydrogen ion” instead of “proton.”
- In the Brønsted-Lowry paradigm, “the equilibrium always favors the formation of *weaker* acids and bases” (Miessler et al., 2014, p. 171).
- Common amphoteric solvents: sulfuric acid, hydrofluoric acid, water, acetic acid, methanol, ammonia, and acetonitrile.
- $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are the strongest acid and base, respectively, that<sup>[2]</sup> can exist in  $\text{H}_2\text{O}$ .
- **Leveling effect:** Acids stronger than  $\text{H}_3\text{O}^+$  cannot be differentiated by their aqueous ionization.
- Because of leveling, the strength of the strong acids cannot be differentiated in aqueous solution.
  - Thus, we use more strongly acidic solvents, such as **glacial** acetic acid.
  - The use of this solvent allows us to determine that  $\text{HClO}_4 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$ .
  - Note that basic solvents similarly permit the differentiation of strong bases.
- **Glacial** (substance): A 100% pure, concentrated sample of a substance.
- “Nonamphoteric solvents...do not limit solute acidity or basicity because the solute does not react with the solvent. In these solvents, the inherent solute acid or base strength determines the reactivity, without a leveling effect” (Miessler et al., 2014, p. 173).
- **Superelectrophilic activation:** The result of generating small organic ions bearing a large amount of positive charge.
- Introduces the Hammett acidity function<sup>[3]</sup>.
- Protonating  $\text{CH}_4$  is of particular interest since the natural abundance of methane (from natural gas) makes it attractive as a starting point for synthesis of more complex molecules.
  - $\text{CH}_5^+$  has been isolated;  $\text{CH}_6^{2+}$  and  $\text{CH}_7^{3+}$  have been proposed.
- Dissolving  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  results in **fuming sulfuric acid**, which contains higher polysulfuric acids such as  $\text{H}_2\text{S}_2\text{O}_7$ , all of which are stronger than  $\text{H}_2\text{SO}_4$ .
- Water is a strong base in superacid media: Adding  $\text{H}_2\text{O}$  to superacids produces hydronium salts.
  - As a consequence, we can form  $[\text{H}_3\text{O}][\text{Ln}][\text{AsF}_6]_3$  where Ln is a lanthanide element as  $\text{AsF}_6$  is part of a superacid.
- Thermodynamic measurements:
  - Hess’s law is often used to express the enthalpy of weak acid reactions in terms of reactions that do go to completion; this is not perfect, but it’s an ok starting point.

<sup>2</sup>Errata: Miessler et al. (2014, p. 173) has a typo: “than” instead of “that.”

<sup>3</sup>Errata: The – sign should be a + sign.

- One can also measure  $K_a$  via titration curves at different temperatures and use the van't Hoff equation

$$\ln K_a = \frac{-\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R}$$

- According to the above equation the plot of  $\ln K_a$  vs.  $\frac{1}{T}$  will be linear with a slope that allows us to determine  $\Delta H$  and a  $y$ -intercept that allows us to determine  $\Delta S$ .
- Brønsted basicity scale: Enthalpy changes associated with protonation by the superacid fluoro-sulfonic acid ( $\text{HSO}_3\text{F}$ ).
- The best measure of acid/base strength is gas-phase acidity/basicity, since there are no solvent effects.
  - Wrt.  $\text{HA}(\text{g}) \longrightarrow \text{A}^-(\text{g}) + \text{H}^+(\text{g})$ ,  $\Delta G$  = Gas-Phase Acidity (GA) and  $\Delta H$  = Proton Affinity (PA).
  - There exist analogous definitions for bases.
  - Modern measurement techniques can measure these values very accurately for a select few molecules; from these molecules and Hess's law, we can build pretty good approximations of other reactions.
- **Superbase**: A base with a gas-phase proton affinity greater than  $1000 \text{ kJ mol}^{-1}$ .
  - Examples such as Grignard and organolithium reagents are ubiquitous in organic synthesis.
- Considers inductive effects.
- "Solvation [of amines] is dependent on the number of hydrogen atoms available to form  $\text{O} \cdots \text{H}-\text{N}$  hydrogen bonds with water" (Miessler et al., 2014, p. 181).
- Steric effects are less obvious — for example, 2,6-dimethylpyridine is more basic than 4-methylpyridine, but the latter is more basic than 2-*t*-butylpyridine.
- Binary hydrogen compounds:
  - Acidity increases left-to-right across a period and down a group (wrt. the non-hydrogen atom).
  - The three heaviest hydrohalic acids are all equally acidic in water due to leveling.
- Considers relative strengths of various chlorine-based oxyacids (e.g.,  $\text{HClO}_4$  vs.  $\text{HClO}_3$ ).
  - As the number of oxygens increases, the electronegativity of the terminal oxygen increases. Less and less electron density binds the hydrogen, making the bond increasingly weak and susceptible to heterolytic cleavage.
- In polyprotic acids, the  $\text{p}K_a$  increases about 5 units with each successive proton removal.
- Aqueous cations get surrounded by  $\text{H}_2\text{O}$ .
  - Then these complexes react in acid-base reactions.
  - When the concentration is sufficiently high, they can two complexes can combine via hydroxide or oxide bridges between the metal atoms.
  - Metal ions with charges of 4+ or higher are the really acidic ones. They're acidic to the extent that they do not exist by themselves in solution, but are present in oxygenated forms such as permanganate ( $\text{MnO}_4^-$ ).
- **Coordinate covalent** (bond): A bond that links a Lewis acid and base into their adduct. *Also known as dative* (bond).
- **Coordination compound**: A Lewis acid-base adduct involving one or more metal ions.
- "In most Lewis acid-base reactions, the HOMO-LUMO combination forms new HOMO and LUMO orbitals of the product" (Miessler et al., 2014, p. 186).



- When the symmetries match and the energies are close, a stable adduct forms.
- Since every molecule has a HOMO and LUMO, technically any molecule can act as acid, base, oxidizing agent, or reducing agent when combined with the right reactants.
  - For example,  $\text{H}_2\text{O}$  can oxidize Ca metal, forming  $\text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) + \text{H}_2(\text{g})$ .  $\text{H}_2\text{O}^{-}$  is not formed because the addition of electrons to antibonding orbitals in  $\text{H}_2\text{O}$  weakens one O–H bond.