

7.2.1: Hard and Soft Acids and Bases

Origin of the Hard-Soft Acid-Base Principle

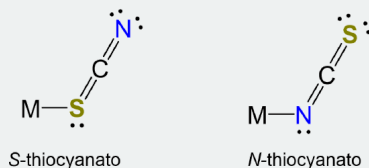
One of the strengths of the Lewis acid-base concept is the readiness with which it illuminates the role that covalent and electrostatic interactions in acid base behavior, specifically through its ability to explain chemical interactions in terms of frontier orbitals and the interactions between charged groups as electrons are donated from a base to an acid. However, simply acknowledging the presence of such interactions does little to illuminate the degree to which each mode of explanation best explains the bonding in a given system? To what extent is a given adduct better described as held together by covalent bonds as opposed to ionic ones - *e.g.* better described as a molecule rather than an ion pair? Moreover, does it even matter, given that the orbitals of quantum mechanics result from the combination of electrons' wavelike behavior with their electrostatic attraction to nuclei in either case? These questions and more are addressed by one of the most important conceptual tools in contemporary inorganic chemistry, the hard-soft acid-base principle.

The hard-soft acid-base (HSAB) principle stems from the recognition that some Lewis acids and bases seem to have a natural affinity for one another.* Consider the following:

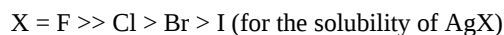
- Some metals are commonly found in nature as salts of chloride or as oxide ores while others are found in combination with sulfur. Geochemists even use the Goldschmidt classification scheme to classify the halide and oxide formers as lithophiles and the sulfide formers as chalcophiles.
- In living systems small highly charged metals ions like Fe^{3+} are usually found bound to N and O atoms while larger metals with lower charges such as Zn^{2+} are often found attached to at least one S atom. Similarly, metals prefer to bind to one coordination site over the other when forming complexes with ambidentate ligands. The most well-known instances involve complexes of cyanate and thiocyanate, which can coordinate metals through either the N or chalcogen atom. For instance, Cu^{2+} and Zn^{2+} form *N*-thiocyanato complexes in species like $[\text{Cu}(\text{NCS})_2(\text{py})_2]$ and $[\text{Zn}(\text{NCS})_4]^{2-}$ while their larger congeners Au^{3+} and Hg^{2+} preferentially forms *S*-thiocyanato complexes, giving species like $[\text{Hg}(\text{SCN})_4]^{2-}$.

Ambidentate ligands

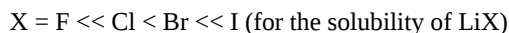
Ambidentate ligands possess multiple coordination sites through which a metal may bind. For instance, thiocyanate may coordinate metals (M) at either the S or N to give *S*-thiocyanato or *N*-thiocyanato complexes.



- The solubility trends for the alkali metal halides and silver halides are opposite, even though both involve salts of formula M^+X^- (salts can be thought of as involving Lewis acid-base adduct formation between the anions and cations). Specifically, although the silver halides are all relatively insoluble in water, the very modest solubility they possess follows the order:



In contrast, the much more ample solubility of the alkali metal halides** follows the opposite order. For example, the order for the lithium halides is



Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

Qualitative HSAB Principle

The hard-soft acid-base principle is a conceptual tool for thinking about patterns of Lewis acid base reactivity. The explanation of the trends in metal distribution, halide salt solubility, and preferred metal coordination patterns is rooted in Arland, Chatt, and Davies' observation that *Lewis acids and bases could be classified into two groups based on their propensity to form stable compounds with one another (e.g. acids in a class tend to form more stable adducts with bases in the same class than they did with bases in the other)*.¹ Arland, Chatt, and Davies somewhat boringly termed these groups class a and class b but today they are known by Ralph Pearson's name for them. Pearson called the class a acids and bases hard and class b acids and bases soft. These terms reflect how "soft" these substance's electron clouds are towards distortion or, in other words, their polarizability (Figure 7.2.1.1). Pearson terms acids and bases which are relatively polarizable **soft** and those which are difficult to polarize **hard**.

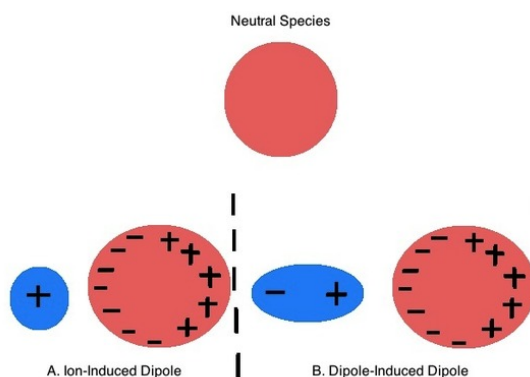


Figure 7.2.1.1: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. An fragment's polarizability determines the degree to which its electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment. The figure is taken from (and the caption expanded from) Cox, Kelly and Dana Reusser "Polarizability" in

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Recognizing Hard and Soft Acids and Bases

Hard acids and bases come in two varieties:

1. hard acid and base sites which possess few valence electrons and for which polarization therefore involves distorting core electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. The most common examples of such substances are Lewis acids hard acids towards the left of the periodic table.
2. hard acids and base sites with a high charge density (highly charged relative to size) and/or which are electron deficient. In these cases polarization involves distorting electrons that already experience strong unshielded electrostatic interactions.

Soft acids and bases also come in two varieties

1. soft acids and bases which possess many valence electrons and so are more readily polarized. In consequence, all other things being equal, soft acids and bases are more likely to be found towards the middle or right of the periodic table.
2. soft acids and bases with little charge density and/or which are relatively electron rich.

Note that the hard-soft classification should not be thought of as if all hard acids and bases are equally hard and all soft acids and bases equally soft. There is a graduation in hardness and softness and a number of intermediate acids and bases which do not fit neatly in either category. With this caveat in mind, representative **hard, soft, and borderline acids** are given below. Notice how they illustrate the trends just outlined.

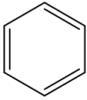
Selected Hard Bases (Class a)

Nitrogen bases	Oxygen bases	small halides
NH_2^-	OH^-	CO_3^{2-}
NH_3	H_2O	RCO_2^-
RNH_2	ROH	NO_3^-
NH_2NH_2	ROR	PO_4^{3-}
		SO_4^{2-}

Selected Borderline Bases

electron-poor Nitrogen bases	low oxidation state element oxyanions	intermediate halides
N_3^-		
NO_2^-	NO_2^-	
SCN^-	SO_3^{2-}	Br^-
N_2		

Selected Soft Bases (Class b)

Carbon bases	P and As bases	Sulfur bases	large halides & pseudohalides
R^-	PR_3	RS^-	H^-
CO	P(OR)_3	RSH	I^-
CN^-	AsR_3	RSR	
RNC		SCN^-	
$\text{R}_2\text{C}=\text{CR}_2$ (alkenes)			
			

(electron-rich aromatics)

Qualitative Estimation of the Relative Hardness and Softness of Lewis Acids and Bases

As can be seen from the examples above, **hard acids are relatively electron-poor and hard bases electron-rich** since they have comparatively

- small frontier orbitals, reflective of their relatively small atom/ion/fragment sizes
- high (for acids) or low (for bases) oxidation states on the base atom, reflected in a large positive formal charge (for acids) or negative formal charge (for bases)
- low polarizability, due to loss or gain of substantial numbers of electrons, or the localization of
 - positive charge on an electropositive element or an atom bearing electron-withdrawing substituents
 - negative charge on an electronegative element or an atom bearing electron-donating substituents

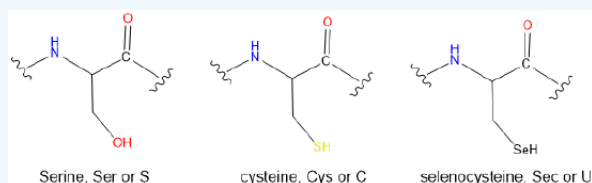
In contrast to hard acids and bases **soft acids are relatively electron-rich and soft bases larger and more electron poor** since they have comparatively

- large frontier orbitals, reflective of their relatively large atom/ion/fragment sizes
- low oxidation states, often resulting in small or nonexistent atomic charges
- high polarizability, as might be expected of species in which electron-electron repulsions are lower and electrons are spread over a large volume. Sometimes this is indicated by
 - positive charge on an electronegative element or an atom bearing electron-donating substituents
 - negative charge on an electropositive element or an atom bearing electron-withdrawing substituents

? Exercise 7.2.1.1

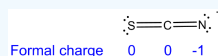
Rank the acid or bases in each set in increasing order of expected hardness?

- Cr^{2+} and Cr^{3+}
- H^+ , Cs^+ , and Tl^+
- SCN^- (acting as a base at N) and SCN^- (acting as a base at S)
- AlF_3 , AlH_3 , AlMe_3
- The side chains of the following proteinogenic amino acids



Answer

- $\text{Cr}^{2+} < \text{Cr}^{3+}$ All other things being equal, hardness increases with oxidation state.
- $\text{Tl}^+ < \text{Cs}^+ < \text{H}^+$ The order reflects Cs^+ and Tl^+ 's larger size relative to H^+ (which doesn't possess any electrons that can be polarized anyway) and that Tl^+ still possesses two valence electrons while Cs^+ possesses none.
- SCN^- (acting as a base at S) $<$ SCN^- (acting as a base at N) The order reflects that N is more electronegative than S and possesses a more negative formal charge of -1.



- $\text{AlH}_3 < \text{AlMe}_3$, AlF_3 The hardness increases as the substituents on the Lewis acid Al center become less electron donating and more electron withdrawing (and, incidentally, harder bases) as their electronegativity increases in the order $\text{H}^- < \text{CH}_3^- < \text{F}^-$. Note that the order of electron donating ability for H^- and CH_3^- is the opposite observed for carbocations, for which hyperconjugation plays a larger role.
- $\text{Sec} < \text{Cys} < \text{Ser}$ The hardness increases as the electronegativity of the Lewis base chalcogen increases on going from a selenol to a thiol to an alcohol.

References

- Ahrland, S.; Chatt, J.; Davies, N. R., The relative affinities of ligand atoms for acceptor molecules and ions. Quarterly Reviews, Chemical Society 1958, 12 (3), 265-276.
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Contributors and Attributions

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