



Lewis acid-base concept – a unifying principle applicable to soil system, geochemistry and biology

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Abstract

The concept of hard and soft Lewis acids and bases was reviewed as a unifying principle in the chemistry of soil system, in the geological distribution of elements and in living systems. The common aquatic character of natural environments with the important role of hard-hard interactions and the factors determining the bond strength were discussed. Further evaluations included the complexation tendency of hard ions in water solution which is parallel with the standard entropy of ions. In the soil system, these principles manifest as increased sorption ability of oxyacid ligands with increasing pKa of the acid, while the complexation of hydrated metal cations is enhanced with decreasing pK of hydrolysis. From mineralogical and metallurgical points of view the softness is expressed as poor hydration of inert noble metals. In biological systems, coordination environments for metals range from very hard oxygen donors to very soft sulphur donors.

Key words: Hard and soft acids and bases, ion-water interactions, nutrient cycle, sorption of ions.

Introduction

Despite the complexity of the chemistry of the inorganic and organic nature, it is possible to find some general trends. The concept of hard and soft acids and bases presents a classification which is widely applicable. It is valuable in answering the question, why some elements or ions prefer to bind to certain elements or ions. The purpose of this paper was to review the Lewis acid-base theory as a unifying principle in soil chemistry, geochemistry and biology. The common environment of chemical reactions in nature being water solution, further discussion was based on the examination of Lewis acid-base reactions in water solution. It is not exaggerated to consider e.g. the soil chemistry essentially to be aquatic chemistry. The availability of plant nutrients or toxicity of detrimental elements are highly dependent on sorption and desorption reactions between soil solution and surfaces of organic and inorganic soil constituents. Nor is it very difficult to find the points in common with geochemistry and plant physiology: chemical weathering delivers ions to the soil solution which is the source of ion uptake for plants.

Lewis Acids and Bases

Any chemical species with an empty electron orbital is a Lewis acid, an electron pair acceptor³. Any chemical species with a lone electron pair is a Lewis base, an electron pair donor³. Reactions in which a coordination bond, more or less covalent, is formed through sharing of an electron pair between a donor base and an acceptor acid are called Lewis acid-base reactions. The difference in the energy of the interacting donor and acceptor orbitals is a measure of ionic character in the bond^{3,16}. The strength of a covalent interaction depends on the extent of overlap of the interacting orbitals.

The stability of the complexes of metal ions is dependent on

the electronic structure, especially on the outer electron shell of the metal ion and the donor base in question. Accordingly, polarizability is one of the most important properties of Lewis acids and bases. A semiempirical correlation classifies Lewis acids and bases as soft or hard according to the ease with which their electron clouds are distorted by the electric field of a nearby atom or ion²². Soft acids are characterized by fairly abundant electrons in the outer orbitals which are screened from the nucleus, whereas hard acids have few, if any, d electrons and a high charge-to-radius ratio, resulting in tightly bound, closely packed electron shells. In soft bases the lone electron pairs are relatively loosely bound to the nucleus of the donor atom, while in hard bases the lone electron pairs are tightly bound to the nucleus. Hard acids tend to form the most stable complexes with hard bases, and soft acids with soft bases²².

A typical hard acid is a small metal cation with high positive charge and without valence electrons (e.g. H⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺ and Si⁴⁺). An increasing oxidation number means a decreasing number of outer electrons, thereby an increasing hardness as well. Accordingly, acids in the zero oxidation state are soft, and the transition metals in low oxidation states are either soft or intermediate acids. Acids with less than five d electrons are hard, but with a higher number of d electrons the soft character of the acid is more obvious⁷. With increasing cation size the polarizability and softness tend to increase.

The most stable complexes of hard acids are formed with ligands with oxygen as the donor atom or with F⁻ and N ligands. These donors with properties of a hard base are characterized by high electronegativity, and they do not possess low-energy, empty electronic orbitals. The simple electrostatic approach is particularly effective for complexes of hard acids^{3,16}.

Soft acids form the most stable complexes with the heavier elements of the N, O and F groups. In complexes of soft acids, crystal field effects lowering the energy state of the complex and covalent bonding are important factors in addition to the simple electrostatic approach^{3,16}. Soft acids possess filled or nearly filled d subshells in their outer shells capable of donating electrons to unfilled π -symmetry orbitals of soft ligands (e.g. P, As, S and I)⁷. The weaker tendency of soft acids to form complexes with hard bases is derived from a strong repulsion between d electrons of soft acid and tightly bound p electron pairs of O or F⁷.

Lewis Acid-Base Reactions in Water Solution

In water solution, protons and other hard cations are complexed with the dominating hard base, H₂O. In order to become complexed with hard cations in water solution, the other ligands must displace water molecules which form the primary hydration sphere of the cation. Displacing of water molecules is facilitated with the increasing ability of the competing ligand to donate an electron pair. In oxygen ligands, an oxygen is the better donor of an electron pair the higher the negative partial charge of the oxygen⁷. In oxyanions the negative partial charge of the donor oxygen increases with decreasing electronegativity of the central atom attached to the oxygen^{4,7}. According to these trends, the pKa values of H⁺ complexes of oxyanions given in Table 1 tend to increase with increasing negative partial charge of the donor oxygen. Oxygen in polar water molecule³ has also a low negative partial charge (Table 1). With decreasing pKa the ability of oxyanions to displace water from primary hydration spheres of cations is impaired.

In water solution, the complexation tendency of hard acids and bases is related to their standard entropy (Table 2). The hard acid nature of cations increases with increasing charge and decreasing radius²². This is also the trend of decreasing standard entropy of cations in water solution⁷. In the electric field of small and highly charged cations, the freedom of water molecules is highly reduced, which is manifested by low standard entropy of cation in water solution. The electrostatic attraction between water dipoles forms an internal structure of water in which small groups of water molecules have an ice-like structure⁸. In water solution, ions, uncharged solutes or charged surfaces break down this structure of water, which means an increase in entropy of water. This entropy increase may exceed the entropy decrease caused by water orientation in the electric field of cations with small charge and relatively large size: K⁺ and monovalent cations greater than K⁺⁸. The tendency of oxyanions to donate an electron pair decreases with decreasing partial charge of oxygen. This means increasing entropy of anions in water solution⁷. Anions with the highest positive value of the standard entropy in water solution, MnO₄⁻, ClO₄⁻, ClO₃⁻, BrO₃⁻ and NO₃⁻ (Table 2), are only weakly hydrated weak donors. In water solution these anions as well as SO₄²⁻ to a lesser extent increase the entropy of water, while F⁻ and HO⁻ strongly arrange water and have low entropy⁸.

Table 1. pKa values of H⁺ complexes and values of partial charge of oxygen for oxygen ligands⁷.

H ⁺ complex	pKa	Oxygen ligand	Partial charge of oxygen
H ₂ O	15.97	HO ⁻	-0.66
HPO ₄ ²⁻	12.44	PO ₄ ³⁻	-0.66
HSiO ₃ ⁻	12	SiO ₃ ²⁻	-0.63
HCO ₃ ⁻	10.22	CO ₃ ²⁻	-0.56
HSO ₃ ⁻	7.2	SO ₃ ²⁻	-0.55
H ₂ PO ₄ ⁻	6.15	HPO ₄ ²⁻	-0.53
HNO ₂	3.35	NO ₂ ⁻	-0.38
H ₂ CO ₃	3.3	HCO ₃ ⁻	-0.33
H ₂ SeO ₃	2.52	HSeO ₃ ⁻	-0.31
H ₃ PO ₄	2.12	H ₂ PO ₄ ⁻	-0.31
HSeO ₄ ⁻	2.05	SeO ₄ ²⁻	-0.44
HSO ₄ ⁻	1.89	SO ₄ ²⁻	-0.44
H ₃ O ⁺	-1.74	H ₂ O	-0.25
HNO ₃	neg.	NO ₃ ⁻	-0.29
H ₂ SO ₄	neg.	HSO ₄ ⁻	-0.27
HClO ₄	neg.	ClO ₄ ⁻	-0.21

In a complexation reaction between a hard acid cation and a hard base anion, the energy released in the formation of the bond between metal cation and ligand is about the same as the energy required to disrupt the hydration shells and the enthalpy change ΔH^0 approximately equals zero²⁹. Thus, the free energy change $\Delta G^0 = \Delta H^0 - T\Delta S^0$ in complexation reactions of hard acids and bases is chiefly dependent on the entropy change ΔS^0 . Reactions in which cations and negatively charged ligands interact to form complexes of lower charge proceed with a greatly increased entropy³ due to the hydration shell disruption. The products with lower charge will produce considerably less order of water.

In water solution, soft acids and bases are poorly hydrated and entropy changes in complexation reactions are relatively small¹⁶. Under these circumstances the free energy change ΔG^0 approximately equals the enthalpy change ΔH^0 which is negative for strong complexation between soft acids and bases²⁹.

Lewis Acid-Base Reactions in Soil System

The Lewis bases in soil include H₂O, oxyanions such as HO⁻, organic anions RCOO⁻, CO₃²⁻, SO₄²⁻, HPO₄²⁻ and PO₄³⁻ and organic N and S electron donors. Cations occurring most abundantly in

Table 2. Values of standard entropy (cal/K mol) for ions and molecules in water at 298 K⁷.

H ₃ BO ₃	21.41	H ⁺	0	Mg ²⁺	-28.2	Al ³⁺	-74.9
NH ₃	26.3	Na ⁺	14.4	Fe ²⁺	-27.1	Cr ³⁺	-73.5
HF	26	Ag ⁺	17.67	Co ²⁺	-27	Fe ³⁺	-70.1
HCOOH	39.1	K ⁺	24.5	Zn ²⁺	-25.5	PO ₄ ³⁻	-5.2
H ₃ PO ₄	42.1	NH ₄ ⁺	26.97	Cu ²⁺	-23.6		
H ₂ CO ₃	45.7	HO ⁻	-2.52	Fe(OH) ²⁺	-23.2		
H ₂ SO ₄	56	F ⁻	-2.3	Mn ²⁺	-20		
		H ₂ BO ₃ ⁻	7.3	Cd ²⁺	-14.6		
		Cl ⁻	13.2	Ca ²⁺	-13.2		
		CH ₃ COO ⁻	20.8	Hg ²⁺	-5.4		
		H ₂ PO ₄ ⁻	21.3	Sn ²⁺	5.1		
		HCOO ⁻	21.9	Pb ²⁺	5.1		
		HSeO ₄ ⁻	22.0	CO ₃ ²⁻	-12.7		
		HCO ₃ ⁻	22.7	HPO ₄ ²⁻	-8.6		
		HSO ₄ ⁻	30.52	S ²⁻	-4		
		NO ₃ ⁻	35.0	SO ₄ ²⁻	4.1		
		ClO ₄ ⁻	43.2	SeO ₄ ²⁻	5.7		
		MnO ₄ ⁻	45.4	CrO ₄ ²⁻	9.2		

soil are protons, alkali and alkaline earth cations as well as Al^{3+} and Fe^{3+} , which belong to the group of hard acids. Under these circumstances H_2O , HO^- and other oxyanions should be preferred as donors relative to Cl^- , S^{2-} and organic N and S electron donors which are most readily complexed with bi- or univalent trace metal cations.

When complexation reactions in soil solution or sorption of ions to surfaces of soil particles are concerned, the principles described previously for reactions in water solution are valid. As compared with interactions of single ions or Lewis acids and bases, the only difference in sorption reactions is that soil particles are sources of many charges or groups involved in Lewis acid-base reactions. Thus, the sorption to soil particles is promoted by favorable entropy change. The sorption reactions are either pure Coulombic interactions between ions and charged surfaces or formation of surface complexes. The charges on oxides and organic matter are localized and connected with functional groups with Lewis acid-base reactivity. The charge of organic matter and oxides is dependent on the sorption of protons⁵. In addition to protons all ions which are complexed to the surface of organic matter or oxides determine the surface charge and belong to the surface structure.

Sorption of anions: According to the hard acid nature of Al^{3+} and Fe^{3+} ²², Al and Fe in hydrated oxides of soil prefer to bind to oxygen-containing ligands, primarily with H_2O and HO^- . The ability of the other ligands to be complexed to the surfaces of oxides is dependent on their ability to displace H_2O and HO^- coordinated to aluminium or iron atoms on the oxide surface. This is associated with their ability to act as electron pair donors which is described by pKa values of H^+ complexes, corresponding to oxygen ligands (Table 1).

Anionic oxygen ligands can be classified on the basis of pKa values into groups of different displacing abilities^{1,15}. The first group includes anions, e.g. NO_3^- or ClO_4^- , unable to displace H_2O and HO^- ¹. The anions of the second group, e.g. sulphate, molybdate and selenite, displace H_2O but not HO^- , the sorption being weak at a pH higher than the zero point of charge of the surface¹. The anions of the third group, e.g. phosphate, silicate and carboxylate, displace also HO^- , likewise belonging to the third group¹. The ligands of the third group can be sorbed at a higher pH than the zero point of charge of the surface and can break oxygen bridges in the structure of the oxide surface, the concentration of the anion being high enough¹². Thus, the displacing ability of anions increases with increasing pKa of the oxyacid.

The sorption of anions is dependent on the pH of the soil solution which determines the degree of dissociation of protons from oxide surfaces and H^+ complexes in solution. At low pH, the proportion of H_2O ligands on oxide surfaces is high²⁶, and mainly H_2O ligands are displaced by anionic ligands. This ligand exchange reaction renders the surface charge more negative, which leads to the lower pH of the zero point of charge on the surface¹¹. With an increasing pH the proportion of H_2O , being displaced more easily, decreases, while the proportion of HO^- increases on the oxide surface.

The pH being much lower than the pKa of monoprotic acid or the pKa₁ of polyprotic acid, the concentration of corresponding anions is low and sorption is weak. With increasing pH the anion

concentration and sorption increase. The sorption of anions peaks near the pH corresponding to the pKa or pKa₁ value¹¹. When pH is further increased, the sorption of anions of a monoprotic acid decreases rather steeply, but the sorption of polyprotic acid anions decreases slowly with breaks in the slope of the envelope at the pH corresponding each pKa value.

In principle, the dissociation of more than one proton increases the ability of an anion to donate an electron pair, and thus the envelope should have a rising slope. The decreasing slope of the envelope indicates the significance of entropic factors. With increasing pH the ability of the acid corresponding to the sorbing anions to deliver protons for neutralization of exchanged HO^- ions decreases, forming the decreasing slope of the envelope. With increasing pH the HO^- ion concentration in the solution as such has an impairing effect on the sorption of the other anions through competition. With an increasing pH the bonding of anions of polyprotic acids is strengthened by the formation of ring structures through the bonding of ligands to two adjacent metal atoms at the same time^{17,25}.

The sorption of anions like phosphate is affected by the ionic strength of the solution. An increase in sorption has been observed with an increasing electrolyte concentration or with increasing charge of electrolyte anions^{13,27,28,32}. This effect may be caused by a decrease in the volume of the diffuse layer, which possibly enhances the anion sorption²⁷. It is also the effect of an increasing cation concentration decreasing repulsion between the negatively charged surface and anions. Cations which can be bound to oxides through Lewis acid-base reactions may increase the positive charge of the surface and enhance the anion sorption^{19,28}. On the other hand, they compete with anions for reaction sites¹⁴.

Sorption of metal cations: The sorption of metal cations on oxides through Lewis acid-base reactions is dependent on the hydrolysis constants of cations (Table 3). When the first proton is dissociated from a hydrated metal cation, its positive charge is lowered and it has a donor oxygen atom. Hence the hydrolyzed metal cation is an oxygen ligand and can be bound to oxide surface. However, with increasing pK₁ values of the hydrolysis reaction (Table 3) the ability of hydrated cations to be sorbed on aluminium and iron oxides is impaired²⁵. Thereby the alkali and alkaline earth cations with high pK₁ of the hydrolysis have a weak tendency to be hydrolyzed or sorbed through ligand exchange.

The high pK₁ value of hydrolysis reaction of hydrated cations is associated with a high standard entropy in water solution which is characteristic of alkali metal cations (Table 2). Inversely, divalent and especially trivalent hydrated metal cations have high negative values of standard entropy in water solution (Table 2). Therefore they have a strong tendency to be hydrolyzed. Through hydrolysis the charge of cation is lowered and entropy increased. A further increase of entropy is caused by polymerization or sorption of hydrolyzed metal cations.

Polymerization, especially concerning trivalent cations, is a Lewis acid-base reaction in which hydrolyzed metal cations are bound through oxygen bridges to each other. When cations of the same metal are connected through oxygen bridges, the tendency of the bonds between cations and bridging oxygen to break is not great, because the electron pairs of oxygen are evenly

Table 3. The first hydrolysis constant for metal ions at 298 K ².

Ion	pK	Ion	pK
K ⁺	14.46±0.4	Zn ²⁺	8.96±0.05
Na ⁺	14.18±0.25	Cu ²⁺	<8
Ca ²⁺	12.85±0.1	Pb ²⁺	7.716±0.1
Ag ⁺	12±0.3	Al ³⁺	4.97±0.02
Mg ²⁺	11.44±0.1	Cr ³⁺	4.0±0.3
Mn ²⁺	10.59±0.04	Sn ²⁺	3.40±0.4
Cd ²⁺	10.08±0.1	Hg ²⁺	3.40±0.4
Ni ²⁺	9.86±0.03	Fe ³⁺	2.19±0.02
Co ²⁺	9.65±0.05	Ti ³⁺	2.2±0.3
Fe ²⁺	9.5±0.1		

distributed between metal atoms. This leads to further polymerization. When ions of two elements are connected through oxygen bridges, the tendency of the bonds between ions and bridging oxygen to break increases, because the electron pairs of oxygen are more strongly attracted by the element of higher electronegativity. This latter case will be the consequence of sorption of ions (other than aluminium or iron ions) to aluminium and iron oxide polymers. Cations involved in exchange reactions with ligands coordinated to the surface of oxides are ions which determine the charge of the oxide surface ^{10,19}. The sorption of cations has a similar effect on the surface charge as the sorption of protons: negative surface charge is decreased or positive charge increased, the zero point of charge of the oxide surface shifting to a higher pH.

In the reactions of metal cations with organic matter the bond strength is dependent on the ability of cations to accept an electron pair from the donor atom and on the ability of the ligand to donate an electron pair. The strength of the bond is a result of the combined effects of these two factors. With increasing ability of a cation to accept an electron pair the pK₁ value of hydrolysis decreases. With increasing ability of the oxygen ligands to donate an electron pair the pKa of corresponding acid increases.

The functional groups of organic matter represent a wide range of pKa values ^{6,18, 20, 21-24, 30, 31}. The higher the pKa, the better a donor the ligand is. The bonding of di- or trivalent cations is also improved by chelation to two adjacent functional groups. With decreasing pH the complexation of metal ions is increasingly hampered through competition for ligands between metal cations and protons. However, entropic factors are favorable for complexation of most di- and trivalent cations (Table 2) with negative standard entropy in water solution, while the standard entropy of H⁺ is zero.

In the formation of a metal complex, coordinated H₂O ligands are displaced by functional groups. With increasing pKa of the functional group its displacing ability increases. However, the displacing of coordinated H₂O is in general easy, except by functional groups with a very low pKa value. Under these circumstances the complexation of cations is affected by the acceptor properties of the cation in question which are described by pK values of hydrolysis. Cations with high pK (e.g. Na⁺) are poorly hydrated, and their tendency to accept electron pairs from other ligands than H₂O is also weak. The increasing ability to accept electron pairs is parallel with increasing hydration and decreasing pK value of the cation hydrolysis. According to these two trends, the most stable complexes are formed by cations with low pK and ligand with high pKa.

Hard and Soft Acids and Bases in Geochemistry and Biology

One field where the principle of hard and soft acids and bases appears in nature is the geochemical distribution of elements. According to Goldschmidt's classification, metallic elements (e.g. ions) which tend to sort preferentially into an oxide environment are called lithophilic and those which prefer a sulphide environment chalcophilic elements ¹⁶. It is evident that the ions of lithophilic elements tend to be identical with hard acids and those of chalcophilic elements with soft acids. In natural, more or less aquatic environments the occurrence of hard and soft metals varies. The hard metal cations are strongly solvated in water, while the hydration energy of soft metal cations is smaller than the bonding energy in the metal, which is expressed in the inertness of soft metals like Au, Ag and Hg ⁷.

Virtually, all biological coordination involves the use of only three donor atoms: oxygen (e.g. carboxylate groups of amino acids, phosphate groups), nitrogen (e.g. nitrogen bases of amino acid side chains, porphyrins) and sulphur (e.g. the sulphur-containing side chains of the amino acids cysteine, cystine and methionine) ¹⁶. These three elements allow the engineering of coordination environments ranging from very hard (all oxygen donors) to very soft (all sulphur donors). The H⁺ ion is competing with the metal cations, and further selectivity is possible through regulation of the pH. In plant nutrition, the ligands fall into three classes ⁹, the first including ether, alcohol and carbonyl-O ligands with an uptake factor favoring K⁺ and Na⁺ ions. The second class includes carboxylate or phosphate-O ligands with Mg²⁺ and Ca²⁺ uptake favored, and the third class N or S donors which favor transition metals. The ligands of all groups must have a low pKa so that they are available at physiological pH.

The metal ions in living systems may be subdivided into two groups ³³. Members of the first group (e.g. H⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) have hard Lewis acid character and are generally quite mobile, experiencing a variety of changing coordination environment. They are usually implicated in such phenomena as energy transport, nerve conduction, the triggering of muscle action and the regulation of osmotic pressure gradients. Members of the second group are generally nonmobile with a relatively fixed coordination environment, acting as prosthetic groups on enzymes serving as an active site by means of which the substrate is bound to and oriented. The cations of the second group are generally borderline or weakly soft acids.

Hard acids and bases are usually the normal, abundantly occurring components of biological systems. An organism will tolerate most hard acids and bases. The most important inorganic poisons are either soft Lewis acids (e.g. Hg²⁺, Pb²⁺, CH₃Hg⁺, Sb³⁺, Cd²⁺) or soft Lewis bases (e.g. CN⁻, CO, H₂S) ¹⁶. Soft Lewis bases are generally lethal in rather small doses, which suggests that they are highly specific in their action ³⁴. They work through masking of active metal sites via coordination, and in higher concentrations they may even extract metal ions from enzymes and metalloporphyrins. Soft Lewis acids are generally less specific. Though they may render enzymes inactive by displacing the normal cation from active sites, they probably interact indiscriminately with S (and to a lesser degree with N) donor sites. The accumulation of metal cation may lead to inactivation of enzymes through masking necessary S donor sites or to precipitation of metal-protein complexes.

Conclusions

The Lewis acid-base concept provides a useful basis for systematization of the reactivity of cations and anions in natural environments at a more or less aquatic character. In organic or inorganic nature, in plant or animal cells as well as in soil system, the same principles of chemical reactivity are valid. In view of water solution reactions, the classification of cations and anions into hard and soft Lewis acids and bases can be interpreted so that the basis for the classification is the ability to be hydrated. The hydration of ions has a considerable influence on the free energy change of complexation reactions which is related to the tendency of a reaction to proceed.

In aqueous environments, a fundamental factor in the reactivity of hard Lewis acids and bases is their entropy in water solution. It is essential that the free energy change in complexation is mainly due to the entropy change, because the bonding energy released is compensated by hydration shell disruption. The entropy values in water solution provide a natural basis for classification of hard acids and bases. With increasing entropy of hard base anions in water solution their ability to donate an electron pair to hard acid cations decreases. The complexation ability of oxyacid anions is impaired with decreasing pK values for dissociation. With decreasing entropy in water solution metal cations have an increasing tendency to be hydrolyzed. With decreasing pK of hydrolysis the complexation ability of cations enhances. In complexation of poorly hydrated soft acids and bases, the free energy change is mainly dependent on the bonding energy.

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