

## 3 Reaction

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Inorganic reactions can be described in terms of redox or acid-base concepts. Thermodynamics and electrochemistry are closely related to the analyses of redox and acid-base reactions. Although it appears that the theories of thermodynamics and electrochemistry are described by a number of complicated equations and formulae, only a few equations and parameters are required for a proper understanding. A good grasp of the sign and trend of the parameters in these key equations greatly helps this understanding. A more detailed understanding beyond this general level can be acquired by building on these basic concepts.

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### 3.1 Thermodynamics

Thermodynamic parameters on changes of state are necessary to describe chemical bonding, structure, and reaction. This is true also in inorganic chemistry, and the most important concepts in thermodynamics are described in this section. Even simple thermodynamic knowledge is considerably useful for judging whether structures of compounds are stable and the likelihood of spontaneous reactions, and for the calculations of reaction heat, determination of reaction mechanism, and understanding of electrochemistry.

**Enthalpy** Since enthalpy is the heat content of a system under constant pressure, the change  $\Delta H$  is negative in an exothermic reaction, and positive in an endothermic reaction. The standard reaction enthalpy,  $\Delta H^0$ , is the enthalpy change between 1 mol of products and reactants in the standard state ( $10^5$  Pa and 298.15 K). The **standard enthalpy of formation**,  $\Delta H_f^0$ , of a compound is the standard reaction enthalpy for the formation of the compound from its constituent elements. Since enthalpy is a state function, the standard reaction enthalpy is calculated by defining the standard enthalpy of formation of simple substances to be zero.

Namely,

$$\Delta H^0 = \sum n \Delta H_f^0 (\text{product}) - \sum n \Delta H_f^0 (\text{reactant})$$

**Entropy** Entropy is a state function, and is a criterion determining whether one state can be reached spontaneously from another state. The 2nd law of thermodynamics states that the entropy,  $S$ , of an isolated system increases upon a spontaneous change. Namely,

$$\Delta S > 0$$

A thermodynamically irreversible process produces entropy. Entropy is related to the disorder of a system in statistical thermodynamics as follows:

$$S = k \ln W$$

$k$  is the Boltzmann constant, and  $W$  is the number of the arrangements of atoms or molecules of the system with the same energy, and corresponds to the extent of disorder. As entropy becomes larger, the larger the disorder of a system.

**Gibbs energy** This quantity is defined as

$$\Delta G = \Delta H - T\Delta S$$

A spontaneous reaction occurs when Gibbs energy of a reaction is negative at constant temperature and pressure. The standard Gibbs free energy  $\Delta G^0$  is related to the equilibrium constant  $K$  of the reaction  $A \xrightleftharpoons{K} B$ .

$$\Delta G^0 = -RT \ln K$$

$K$  is larger than 1 when  $\Delta G^0$  becomes negative, and the reaction proceeds to the right.

### 3.2 Electrochemistry

The **standard state** is defined as the one corresponding to 25°C (298.15 K), unit activity for all the substances in an electrochemical zero-current cell under 1 bar of pressure ( $10^5$  Pa). For a reaction in which  $H^+$  ions participate, the standard state is pH = 0 (approximately 1 mol acid).

In the hydrogen electrode used as the standard of electrode potential, 1 atm of hydrogen gas ( $a_{H^+} = 1$ ) is slowly contacted with a platinum-black electrode immersed in a strong acid solution of activity  $a_{H_2} = 1$ . The potential is expressed as

$$E = E^0 + \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{a_{\text{H}_2}}$$

and by definition  $E^0 = 0$  in the standard state. The hydrogen electrode in the standard state is called the **standard hydrogen electrode**, or NHE. Although reduction potential is usually expressed with reference to the NHE standard, the hydrogen electrode is inconvenient to handle. Therefore a **saturated calomel (SCE)** or an Ag / AgCl electrode is used as a reference electrode for everyday electrochemical measurements and experimental potentials are measured against these electrodes or converted into NHE values. When the NHE value is set to 0, the SCE value is 0.242 V, and the Ag/AgCl value is 0.199 V.

A redox reaction takes place only when redox partners exist and a reactant can be either an oxidant or reductant depending on its reaction partner. The relative redox capability can be expressed numerically by introducing the reduction potentials  $E^0$  of imaginary half-reactions (Table 3.1). The free energy change  $\Delta G^0$  of a reaction is related to  $E^0$ ,

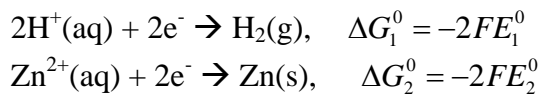
$$\Delta G^0 = -nFE^0$$

where  $n$  is the number of transferred electrons and  $F$  the Faraday constant  $96500 \text{ Cmol}^{-1}$ .

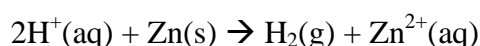
**Table 3.1** Standard reduction potentials at 25 °C

Couple	$E^0 / V$
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.77
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.72
$\text{MnO}_2^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.09
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	+0.15
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.45
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04

For example, the two reactions



do not occur independently, but if both  $\text{H}^+(\text{aq})$  and  $\text{Zn}(\text{s})$  are present, the redox reaction takes place. The equation for the actual reaction is complete when the latter equation is subtracted from the former.



The free energy change of the whole redox reaction is the difference between  $\Delta G_1^0, \Delta G_2^0$  for the respective half-reactions.

$$\begin{aligned}\Delta G^0 &= \Delta G_1^0 - \Delta G_2^0 \\ &= -2F(E_1^0 - E_2^0)\end{aligned}$$

Because half-reactions are not real and they are used in pairs, the free energy change  $\Delta G_1^0$  of  $\text{H}^+$  is set to zero for convenience. Since the experimental value of  $\Delta G^0$  is -147 kJ,  $\Delta G_2^0$  equals 147 kJ. Potential  $E^0$  corresponding to  $\Delta G^0$  of a half-reaction is called the **standard reduction potential**.

$$E^0 = -\frac{\Delta G^0}{nF}$$

Therefore,

$$\begin{aligned}E^0(\text{H}^+, \text{H}_2) &= 0 \quad (\text{by definition}) \\ E^0(\text{Zn}^{2+}, \text{Zn}) &= \frac{-147 \text{ kJmol}^{-1}}{2 \times 96500 \text{ Cmol}^{-1}} = -0.76 \text{ V}\end{aligned}$$

(1 J = 1 CV).

The standard potentials of various half-reactions are determined using similar procedures to that mentioned above (Table 3.1). The  $E^0$ s of redox reactions can be calculated by combining  $E^0$  of these half-reactions.

If  $E^0$  of a redox reaction is positive,  $\Delta G^0$  is negative and the reaction occurs spontaneously. Consequently, instead of the free energy change the difference in reduction potentials can be used to judge the thermodynamic spontaneity of a reaction. The higher the reduction potential of a reagent the stronger its oxidation ability. The

positive or negative signs are based on the expedient of setting the reduction potential of a proton to 0, and it should be understood that a positive sign does not necessarily mean oxidizing, and a negative sign reducing. The series arranged in the order of redox power is called the **electrochemical series**.

### 3.3 Oxidation and reduction

#### (a) Oxidation number

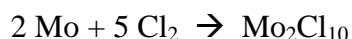
The **oxidation number** is the formal electrical charge of a component atom in a compound or in an ion allocated in such a way that the atom with smaller electronegativity has a positive charge. Since electrical charges do not differ in the case of a molecule composed of the same atoms, the oxidation number of the atoms is the quotient of the net electrical charge divided by the number of atoms. In the case of a compound or an ion consisting of different atoms, the atoms with larger electronegativity can be considered as anions and those with smaller electronegativity as cations. For example, nitrogen is 0 valent in  $N_2$ ; oxygen is -1 in  $O_2^{2-}$ ; nitrogen is +4 and oxygen -2 in  $NO_2$ ; but nitrogen is -3 and hydrogen +1 in  $NH_3$ . That is, the oxidation number can be different for the same atom combined with different partners and the atom is said to be in the formal oxidation state corresponding to that oxidation number. Although this does not express the quantitative deviation of the actual electric charge, it is convenient in counting valence electrons or in dealing with redox reactions.

**Exercise 3.1** Which halogen has the largest oxidizing power?

[Answer] Since the reduction potential of fluorine is the highest, its oxidizing power is the largest.

#### (b) Redox reactions

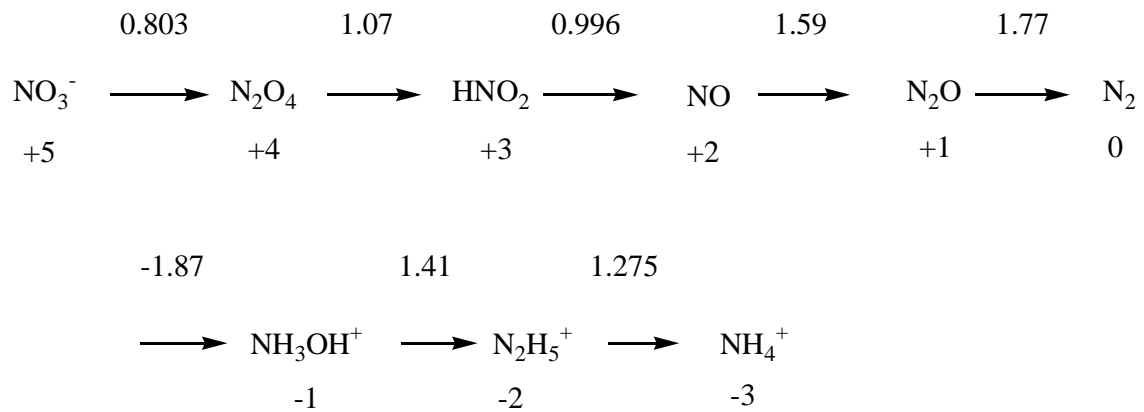
Originally, oxidation meant the formation of oxides from elements or the formation of compounds by the action of oxygen, and reduction is the reverse of oxidation. The present definition of **reduction** is a reaction which gives an electron, and **oxidation** is the reaction which takes an electron. Therefore, a reagent which gives an electron is a **reductant** and one which takes an electron is an **oxidant**. As a result of a redox reaction, a reductant is oxidized and an oxidant is reduced. For example, in the reaction of molybdenum metal and chlorine gas to form molybdenum pentachloride,



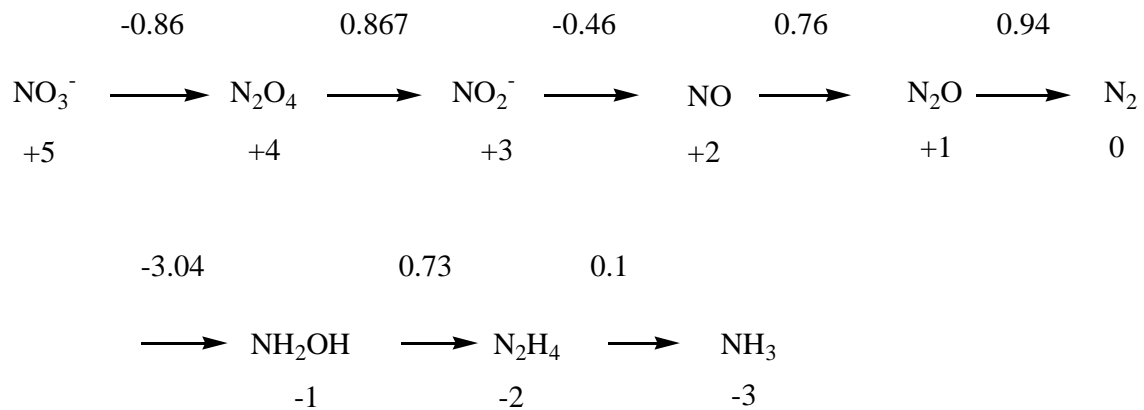
molybdenum is a reductant and changes its oxidation state from 0 to +5 and chlorine is an oxidant and changes its oxidation state from 0 to -1.

**(c) Latimer diagram**

A **Latimer diagram** is a diagram in which the chemical species in the highest oxidation state is placed at the left end and a series of the reduced chemical species of the same atom are arranged to the right-hand side in the order of the oxidation states, and the standard reduction potentials ( $V$ ) are written above the line which connects each state. This diagram is convenient for discussing a redox reaction. Since electric potential differs between an acidic and a basic solution, different diagrams are required depending on the pH of the solution. Taking the series of the oxides and hydrides of nitrogen in acidic solution as an example, ,



in a basic solution, the series becomes



The additivity of the state function  $\Delta G^0$  is used in order to calculate the standard reduction

potential between remote oxidation states.

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0$$

$$-(n_1 + n_2)FE^0 = -n_1FE_1^0 - n_2FE_2^0$$

Where the free energy change and electric potential between adjacent states are  $\Delta G_1^0$ ,  $E_1^0$ ,  $\Delta G_2^0$ ,  $E_2^0$ , respectively, and the number of transferred electrons  $n_1$ ,  $n_2$ .

Namely,

$$E^0 = \frac{n_1E_1^0 + n_2E_2^0}{n_1 + n_2}$$

For example, in the reduction of  $\text{NO}_3^-$  to  $\text{HNO}_2$ , two electrons are transferred to form  $\text{HNO}_2$  via  $\text{N}_2\text{O}_4$  and the potential becomes

$$E^0 = \frac{0.803 \text{ V} + 1.07 \text{ V}}{2} = 0.94 \text{ V}$$

**Exercise 3.2** Calculate the reduction potential of the reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  in a basic solution.

$$[\text{Answer}] E^0 = \frac{-0.86 \text{ V} + 0.867 \text{ V}}{2} = 0.004 \text{ V}$$

In recent years, whenever a new inorganic compound is synthesized, its redox properties are investigated, usually by electrochemical measurements. **Cyclic voltammetry** is the technique of choice for the study of its redox properties, including the electric potential, the number of transferred electrons, and the reversibility of the reactions, *etc.* because of the simplicity of the measurements. It is approximately correct to consider that the oxidation potential corresponds to the energy level of the HOMO, because oxidation usually takes an electron from the HOMO and the reduction potential to the level of the LUMO since reduction adds an electron to the LUMO. However, various factors, such as solvent effects, should be taken into consideration during quantitative discussions of redox processes.

### 3.4 Acid and base

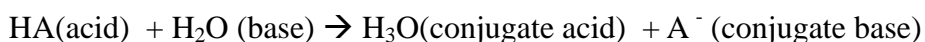
The definition of acid and base has changed over the course of time. This is not a problem of the orthodoxy of one definition but of the convenience of applying the concept to a particular chemical problem. Therefore, ranking the strength of acids and bases also depends on the definition of acid and base used.

#### (a) Arrhenius's acid and base

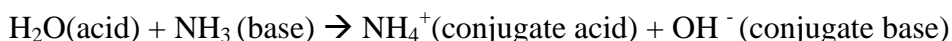
In 1884, Arrhenius defined that an **acid** is a substance that gives  $H^+$  and a **base** one that gives  $OH^-$ . Namely, if an acid is  $HA$  and a base  $BOH$ , then  $HA \rightarrow H^+ + A^-$  and  $BOH \rightarrow B^+ + OH^-$ . Therefore, when an acid and a base react, water is formed.

#### (b) Brønsted-Lowry's acid and base

In a new theory submitted in 1923 independently by Brønsted and Lowry, an acid is defined as a molecule or an ion which gives  $H^+$  and a molecule or ion that receives  $H^+$  from a partner is a base. A base is not only a molecule or an ion which gives  $OH^-$  but anything which receives  $H^+$ . Since the acid  $HA$  gives  $H^+$  to water in an aqueous solution and generates an **oxonium ion**,  $H_3O^+$ , water is also a kind of base according to this definition.



Here  $H_3O^+$  is called a **conjugate acid** and  $A^-$  a **conjugate base**. However, since water gives  $H^+$  to ammonia and generates  $NH_4^+$ , it is also an acid, as is shown below.



That is, water can be an acid or a base dependent on the co-reactant.

Although the definition of Brønsted-Lowry is not much different from that of Arrhenius for aqueous solutions, it is more useful because the theory was extended to non-aqueous acids and bases.

**Exercise 3.3** Write the molecular formulae of nitric acid, perchloric acid, sulfuric acid, and phosphoric acid as oxo acids together with the formal oxidation number of the central atom.

[Answer] nitric acid  $(HO)N^{5+}O_2$ , perchloric acid  $(HO)Cl^{7+}O_3$ , sulfuric acid  $(HO)_2S^{6+}O_2$ , and phosphoric acid  $(HO)_3P^{5+}O$ .

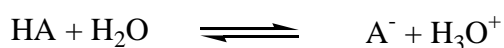


### Acid strength

A protonic acid gives  $H^+$  to water and generates the oxonium ion  $H_3O^+$ . The strength of an acid in a dilute aqueous solution is estimated from the equilibrium constant  $K_a$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

for the dissociation equilibrium,



but it is more convenient to use,

$$pK_a = -\log K_a \quad \text{or} \quad pH = -\log[H_3O^+]$$

An acid with  $pK_a < 0$  is classified as a strong acid and one with  $pK_a > 0$  a weak acid. The conjugate base of a strong acid is a weak base. The  $pK_a$  values of typical acids at 25 °C are shown in Table 3.2.

**Table 3.2** Acidity constants for aqueous solutions of acids at 25 °C.

Acid	$pK_a$
HF	3.17
HCl	-8*
HBr	-9*
HI	-10*
$H_2CO_3$	6.35
$HClO_4$	<0
$HNO_3$	<0
$H_3PO_3$	1.5
$H_3PO_4$	2.15
$H_2SO_4$	<0
$CH_3COOH$	4.56
$C_6H_5COOH$	4.00
$NH_4^+$	9.25
$C_5H_5NH^+$	5.25

\* Estimated value

Since a solvent also works as an acid or a base, the acidity and its range depend on the solvent dissolving the acid. Full dissociation of an acid stronger than  $\text{H}_3\text{O}^+$  gives  $\text{H}^+$  to water, forming  $\text{H}_3\text{O}^+$  in an aqueous solution. For example, both  $\text{HBr}$  and  $\text{HI}$  dissociate completely to become  $\text{H}_3\text{O}^+$ , and their acidities are similar. This kind of phenomenon is called the **leveling effect**, and all acidities become equal to that of  $\text{H}_3\text{O}^+$ . In measuring the relative acidity of strong acids, it is necessary to use a solvent whose  $\text{H}^+$  affinity is smaller than that of water, such as acetic acid or ethanol.

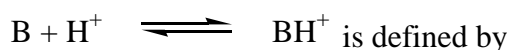
Binary halo acids  $\text{HX}$ , except for  $\text{HF}$ , are very strong acids. Although the  $\text{H}_3\text{O}^+$  concentration itself is also high in an aqueous solution of  $\text{HF}$ , the stronger hydrogen bond of  $\text{F}^-$  compared with that of other halide anions decreases the thermodynamic activity of  $\text{H}_3\text{O}^+$ .

The acidity of oxo acids, such as phosphoric acid, sulfuric acid, nitric acid, and perchloric acid, is related to the formal oxidation number of P, S, N, and Cl. Namely, if the oxo acid  $\text{H}_n\text{XO}_m$  is denoted by  $(\text{HO})_n\text{XO}_{m-n}$ , the positive charge on X becomes positive  $(2m-n)$ , and the acidity is higher for larger value of this number. The number parallels the ease of dissociation of  $\text{OH}$  to give a proton. Acidity is higher in the following order: perchloric acid  $(\text{HO})\text{ClO}_3 >$  sulfuric acid  $(\text{HO})_2\text{SO}_2 >$  nitric acid  $(\text{HO})\text{NO}_2 >$  phosphoric acid  $(\text{HO})_3\text{PO}$ . Although phosphoric acid can be written as  $(\text{HO})_3\text{PO}$ , phosphorous acid is not  $(\text{HO})_3\text{P}$  but  $(\text{HO})_2\text{HPO}$ , and has an acid strength comparable to phosphoric acid.

### Hammett acidity function

Hydrogen ion concentration and pH are meaningful only in dilute aqueous solutions of acids. The acidity in nonaqueous and concentrated solutions is measured using the **Hammett acidity function**. This function makes it possible to measure the acidities of various acids in a non-aqueous solvent or of an acid in various non-aqueous solvents.

The Hammett acidity function in the equilibrium,



$$H_0 = \text{p}K_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]}$$

In a very dilute solution

$$K_{\text{BH}^+} = \frac{[\text{B}][\text{H}^+]}{[\text{BH}^+]} \text{ and}$$

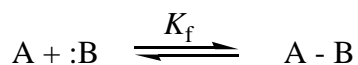
$$H_0 = -\log \frac{[B][H^+]}{[BH^+]} - \log \frac{[BH^+]}{[B]} = -\log[H^+] = \text{pH}$$

An acid with  $-H_0$  over 6 is called a **superacid**. This is an acid that is  $10^6$  times stronger than a 1 molar solution of a strong acid.  $-H_0$  for pure sulfuric acid is 12.1, 21.1 for a solution of HF in  $\text{SbF}_5$ , and 26.5 for the combination of  $\text{HSO}_3\text{F}$  and  $\text{SbF}_5$ .

Superacids have the ability to remove  $\text{H}^-$  from a hydrocarbon and perform H-D exchange and C-C bond scission, *etc.*

### (c) Lewis acid and base

Whereas the concept of Brønsted acid and base is limited to the transfer of protons, a Lewis acid A is generally defined as an acceptor, and a Lewis base B a donor, of an electron pair. An acid A and a base  $:\text{B}$  bind together to form an adduct  $\text{A}:\text{B}$ . For example, a Lewis acid  $\text{BF}_3$  and a Lewis base  $\text{OEt}_2$  (diethylether) form an adduct  $\text{F}_3\text{B}:\text{OEt}_2$ . The stability increases by the completion of an octet around boron when such an adduct forms. The stability of an adduct is expressed by the equilibrium constant of the reaction



$$K_f = \frac{[\text{A}:\text{B}]}{[\text{A}][:\text{B}]}$$

Therefore, the Lewis acidities of a series of acids are measured by comparing  $K_f$  against a common base  $:\text{B}$ . Since a proton is also an electron acceptor, Brønsted acids are the special case of the more general Lewis definition of acids. According to this definition, a co-ordinate bond in a transition metal complex is also an acid-base reaction of a ligand (Lewis base) with a metal center (Lewis acid).

V. Gutmann proposed the negative enthalpy of formation ( $\text{kcal mol}^{-1}$  unit) of the adduct ( $\text{Cl}_5\text{Sb}-\text{Sol}$ ) of Sol (solvent) with a standard acid ( $\text{SbCl}_5$ ) in dichloroethane as a measure of the Lewis basicity of a solvent. This is called the **donor number** (D.N.) of a solvent. On the other hand, the  $^{31}\text{P}$  NMR chemical shift of  $\text{Et}_3\text{P}$  in a solvent is defined as the measure of the Lewis acidity of the solvent and is called the **acceptor number** (A.N.).

### Hard and soft acids and bases

R. G. Pearson classified Lewis acids and bases according to their **hardness and**

**softness.** This classification is an extension of the original theory of S. Ahrlund, J. Chatt, and N. R. Davies, who proposed that metal cations were classified in the order of the stability constants  $K_f$  of the formation of the complexes of the metal cations with halide anions. Namely, the order of  $K_f$  is  $I < Br < Cl < F$  toward metal ions belonging to class *a*, and  $F < Cl < Br < I$  toward those of class *b*. The class *a* type metal cations are hard acids, and class *b* type ones are soft acids. The metal cations which are not much dependent on the kind of halogens have **borderline** character.

What should be noticed here is that  $K_f$  tends to become large for the combination of a hard acid and a hard base, or a soft acid and a soft base. If the concept is extended from simple metal cations and halide anions to general Lewis acids and bases, they can similarly be classified in terms of the hard and soft acid-base affinity. Typical hard acids and bases, and soft acids and bases are shown in Table 3.3.

**Table 3.3** The classification of Lewis acids and bases

	Hard	Borderline	Soft
Acids	$H^+, Li^+, Na^+, K^+$ $Be^{2+}, Mg^{2+}, Ca^{2+}$ $Al^{3+}, Ti^{4+}, Cr^{3+}$ $Fe^{3+}, BF_3, Cl^{7+}$	$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$ $Zn^{2+}, Sn^{2+}, Pb^{2+}$ $Sb^{3+}, Bi^{3+}$	$Cu^+, Ag^+, Au^+$ $Tl^+, Cd^{2+}, Hg^+, Hg^{2+}$ $Pd^{2+}, Pt^{2+}, Pt^{4+}$
Bases	$NH_3, H_2O, R_2O$ $F^-, OH^-, O^{2-}$ $NO_3^-, SO_4^{2-}, PO_4^{3-}$	$N_3^-, N_2, NO_2^-$ $Br^-$ $SO_3^{2-}$	$H^-, CN^-, R^-$ $I^-$ $PR_3, SR_2, CO$

The qualitative expression “softness” is a chemical paraphrasing of the ease of polarization and the larger contribution of covalency than ionicity in bonding. The cations of alkali and alkaline earth metals as well as aluminum are hard and the cations of mercury, copper, silver, and gold, *etc.* are soft. Whereas oxides are hard, sulfides and phosphorus compounds are soft. In the minerals of the Earth’s crust, aluminum, which is hard and oxophilic is found as an oxide, and cadmium, which is soft and chalcophilic is found as a sulfide.

**Exercise 3.4** Applying the concept of hard and soft acids for ferric and ferrous ions, what kind of minerals are expected in iron ores?

[Answer]  $Fe^{3+}$  is a hard acid and  $Fe^{2+}$  is a borderline acid. Therefore, it is likely that the main iron ores are oxide minerals. Although the main ores are actually the oxides hematite  $Fe_2O_3$  or magnetite  $Fe_3O_4$ , a  $Fe^{2+}$  sulfide pyrite  $FeS_2$  is also widely distributed.

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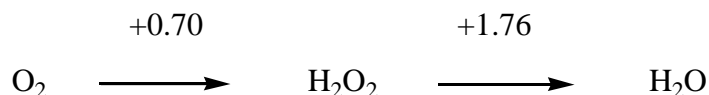
## Acid-base and oxidation-reduction

Some people confuse acid-base and redox reactions. This confusion may be caused firstly by the similar terms originating from oxygen and secondly by misunderstanding about electron transfer. Historically, A. L. Lavoisier, who was one of the great founders of modern chemistry in the 18th century, considered that oxygen was the basis of all acids. He also defined oxidation as the formation of oxides from an element and oxygen. It then took a long time before the present definitions of acid-base and redox reactions were proposed and the old definitions were no longer satisfactory. Furthermore, the Lewis acid accepts an electron pair from a base forming a Lewis acid-base complex, and the oxidizing agent accepts electrons from a reducing agent and is reduced. The fact that acids and oxidizing agents are electron acceptors, and that bases and reducing agents are electron donors, is one of the causes of this confusion.

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### Problem

**3.1** The Latimer diagram of oxygen is shown below. Write the oxidation number of oxygen in each compound.



Calculate the reduction potential of the reaction which converts an oxygen molecule to water, and judge whether this reaction is a spontaneous reaction.

**3.2** Which is the stronger base, ammonia or pyridine?

**3.3** The order of the Lewis acidity of boron halides is  $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ . Is this order reasonable from the standpoint of the electronegativities of halogens?