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CONCEPTUAL CONTRIBUTIONS

A simple unified explanation of the red-ox and acid-base concepts

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Some classical examples of the habitual physico-chemical processes are studied and a unifying conclusion is reached. In the red-ox processes, the atoms or groups of atoms which gain electrons according to their respective oxidation numbers are *oxidizing*, i.e. if the bindings are considered pure ionic, and in the acid-base processes the atoms or groups of atoms which only gain electrons according to their formal charge are *acids*, i.e. if the bindings are considered pure covalent.

Key words: Acid-base, red-ox, Electronegativity, Oxidation number, Formal charge.

The understanding of the red-ox and acid-base chemical reactions is fundamental in explaining a large number of biochemical processes. Red-ox reactions are of great interest in energy transduction processes (i. e., photosynthetic and mitochondrial electron-transport chains); acid-base reactions are very significant in cell pH regulation, O_2/CO_2 transport in respiration, enzyme catalysis, etc.

In this paper we propose a simple, short and unified explanation of these chemical concepts, that may be useful for Biochemistry teachers and students.

In summary,

in red-ox processes *oxidants* are those atoms or ions that, according to their *oxidation number,* gain electrons.	in acid-base processes *acids* are those atoms or ions that, according to their *formal charge,* gain electrons.

Let us start by remembering the definition of a few relevant essential concepts.

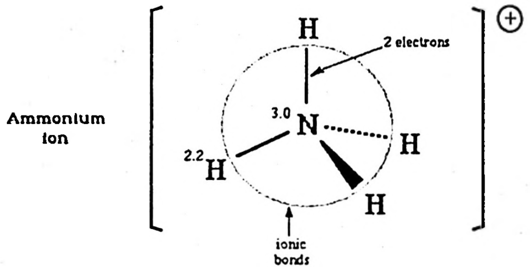
Electronegativity of the atomic elements is a measure of their affinity for electrons. The most electronegative atom has a tendency towards taking electrons from other less electronegative atoms, and in so doing it can form fully or partially *ionic bonds.* Table I shows the electronegativity values of several elements commonly used in Biochemistry (slightly modified from Pauling) (2).

Oxidation number of an atom or an ion is the difference between the number of electrons that this element retains considering that all its bonds with other atoms in a molecule are *ionic bonds* (*i.* e., that the electrons are completely transferred from one atom to the other) and the number of electrons that it possesses in the fundamental state (i. e., the number of its group in the Periodic Table (table I). The negative charge of the electrons has to be considered in the subtractions, and so the calculated number will be negative if there is an excess of electrons and positive if there is a lack of them.

A first example taken to illustrate the method is the ammonium ion (NH_4^+), which has great importance in biochemistry (fig. 1). Since the nitrogen and hydrogen atoms have respectively electronegativities of 3.0 and 2.2 (table I), if

Table I. *Electronegativity of some important atoms in Chemistry and/or Biochemistry.*

Groups						
1	2	3	4	5	6	7
H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
Metals ≤ 1.8 (Fe 1.4)						



Atoms	Electrons in the last level		Fundamental state	Oxidation number
N	8	-	5	= 3 (-)
H	4 x [0	-	1]	= 4 [1(+)]
NH_4^+	Global charge			= 1 (+)

Fig. 1. *Oxidation numbers of atoms in the ammonium ion.*
Bonds are considered to be 100% ionic. In all the chemical formulae presented in this paper each dash represents two electrons (1). If the dash is around the atom it represents its own electrons in the higher atomic orbitals (or last electronic level), and if the dash links two atoms it indicates a bond where each atom shares one electron. When the bond is condidered as an ionic bond then the two electrons of the dash are assigned to the most electronegative atom (indicated with a dotted line close to the atom that donates the electron). If the bond is between two atoms with the same electronegativity or it is considered as a covalent bond, each atom shares one electron of the bond (indicated with a dotted line that cuts the dash in the middle).

the bonds were ionic, N should take all the electrons to complete its last orbital, i. e., 8 electrons. But, because N is an element of the 5th group it will have a surplus of 3 electrons. Therefore, its oxidation number will be -3. At the same time, the hydrogen atom, H, will have a number of oxidation of + 1 (fig. 1). The global charge of the ammonium ion (NH_4^+) calculated in this way will be +1.

Red-ox processes

Figure 2 shows, in a schematic way, three red-ox reactions of interest in biochemistry. It is well known that any

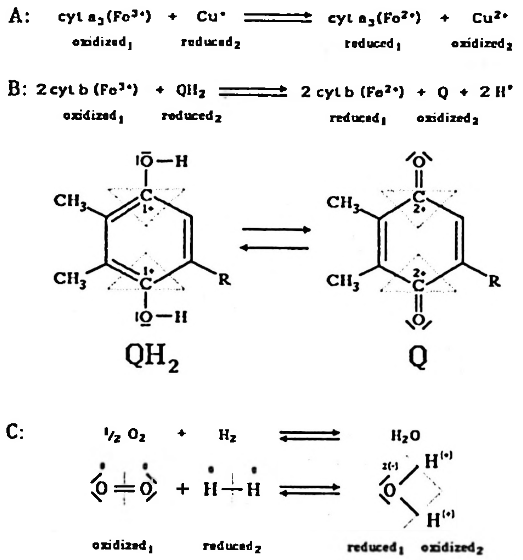


Fig. 2. *Three examples of redox reactions of biological interest.*
The electric charges assigned to the more representative atoms correspond to their respective oxidation numbers. See also legend to fig. 1.

red-ox process can be considered as a binary equation:

$$\text{oxidized}_1 + \text{reduced}_2 \rightarrow \text{reduced}_1 + \text{oxidized}_2$$

The first reaction (fig. 2A) considers a simple electron transfer reaction between two metal ions, Fe and Cu, involved in the respiratory electron transport chain. The change in the oxidation number is quite easily deduced: Fe(+3) → Fe(+2) and Cu(+1) → Cu(+2).

In the second reaction (fig. 2B) the electrons are donated by plastoquinone, a component of the photosynthetic electron transport chain. The figure shows that the atoms that change their oxidation number in the molecule are carbons C_1 and C_4 which move from +1 in QH2 (quinol form) to +2 in Q (quinone form). The other atoms in the molecule do not change their oxidation numbers.

The third reaction (fig. 2C) considers the formation of water from its elements H_2 and O_2 This reaction takes place continuously in the mitochondria being the last red-ox process in respiration, an essential step in the production of free energy from the oxidative catabolism in aerobic living organisms. The figure shows how oxygen is reduced (decreases its oxidation number from 0 to -2), and hydrogen is oxidized (its oxidation number changes from 0 to +1).

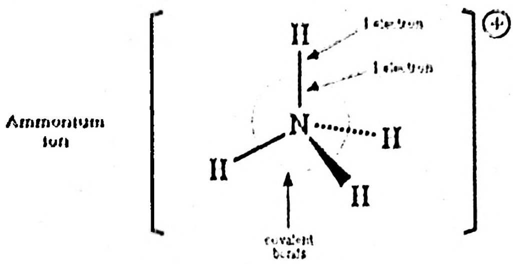
Looking at these examples we can conclude that in a red-ox process the atom or ion that is <u>oxidized</u> *increases* its oxidation number (i.e., it earns positive charges or loses electrons). And the atom or ion that is <u>reduced</u> *decreases* its oxidation number.

Formal charge of an atom or an ion is the difference between the number of electrons that this element retains considering that all its bonds with other atoms in a molecule are <u>covalent bonds</u> (*i.e.*, that each pair of electrons in a bond are mutually shared by one atom and the other) and the number of electrons that it possesses in the fundamental state (i.e., the number of its group in the Periodic Table, see table I). Examples of calculations of formal charges are presented in figure 3. Let us consider again the ammonium ion (NH_4^+), but now looking at the bonds as covalent ones. The nitrogen atom has 4 electrons in the highest level. The number of electrons in its fundamental state is 5, because N is an element of the 5th group. Therefore, its formal charge will be +1. At the same time, each hydrogen atom will have a formal charge of 0 (fig. 3). The global charge of the ammonium ion (NH_4^+) calculated in this new way will again be +1.

Acid-base processes

Figure 4 shows a series of six examples of acid-base reactions. The binary equation for an acid-base process is:

$$\text{acid}_1 + \text{base}_2 \rightarrow \text{base}_1 + \text{acid}_2$$



Atoms	Electrons in the last level		Fundamental state	Formal charge
N	4	-	5	= 1 (+)
H	4 x [1	-	1]	= 4 x [0]
NH_4^+		Global charge		= 1 (+)

Fig. 3. *Formal charges of atoms in the ammonium* ion. Bonds are considered to be 100% covalent. See also legend to fig. 1.

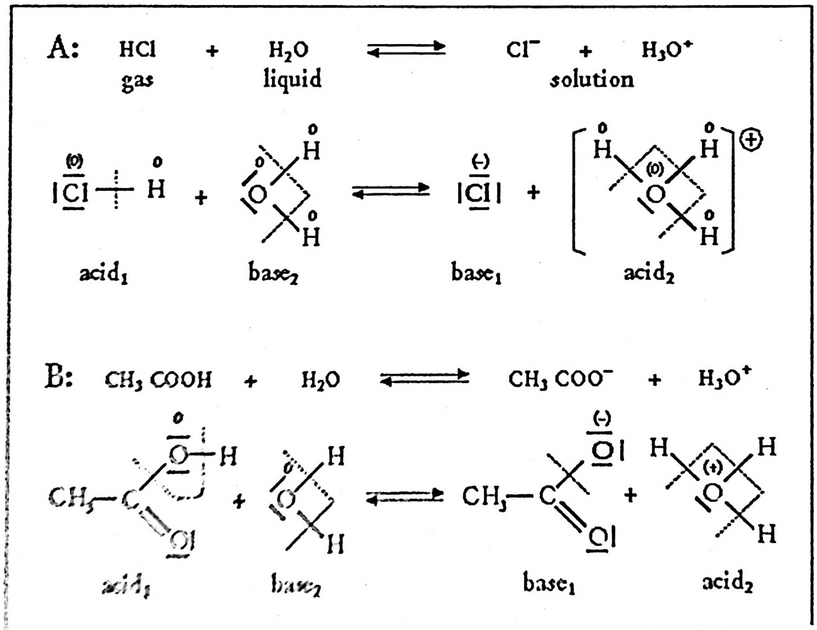
The first reaction (fig. 4A) corresponds to hydrogen chloride in gas phase being dissolved in water and producing hydrochloric acid. The chloride atom maintains its oxidation number (-1) along the process without change. But its formal charge moves from 0 for the hydrogen chloride in gas phase to -1 for the chloride ion. Therefore, since there is a decrease in its positive formal charge, this atom is the acid. However, the oxygen atom in water also presents a stable oxidation number equal to -2 but its formal charge is 0 in neutral water and +1 in the hydronium ion (H_3O^+). Here water behaves as the base (fig. 4).

In the second example (fig. 4B) the reaction of acetic acid with water is shown. One oxygen atom of the acetic acid changes its formal charge from 0 to -1, and the one of water goes from 0 to +1. The remaining atoms do not suffer any modification in its formal charges.

Fig. 4C describes the reaction of ammonium (NH_3) with water. The formal charge of N changes from 0 to +1 and the atom of O in water changes from 0 to -1. In this case water behaves as an acid.

Two other examples are the reaction of boron trifluoride with ammonium (fig. 4D) and the reaction of sodamine with ammonium chloride (fig. 4E).

Looking at these examples we can conclude that in an acid-base process the acid



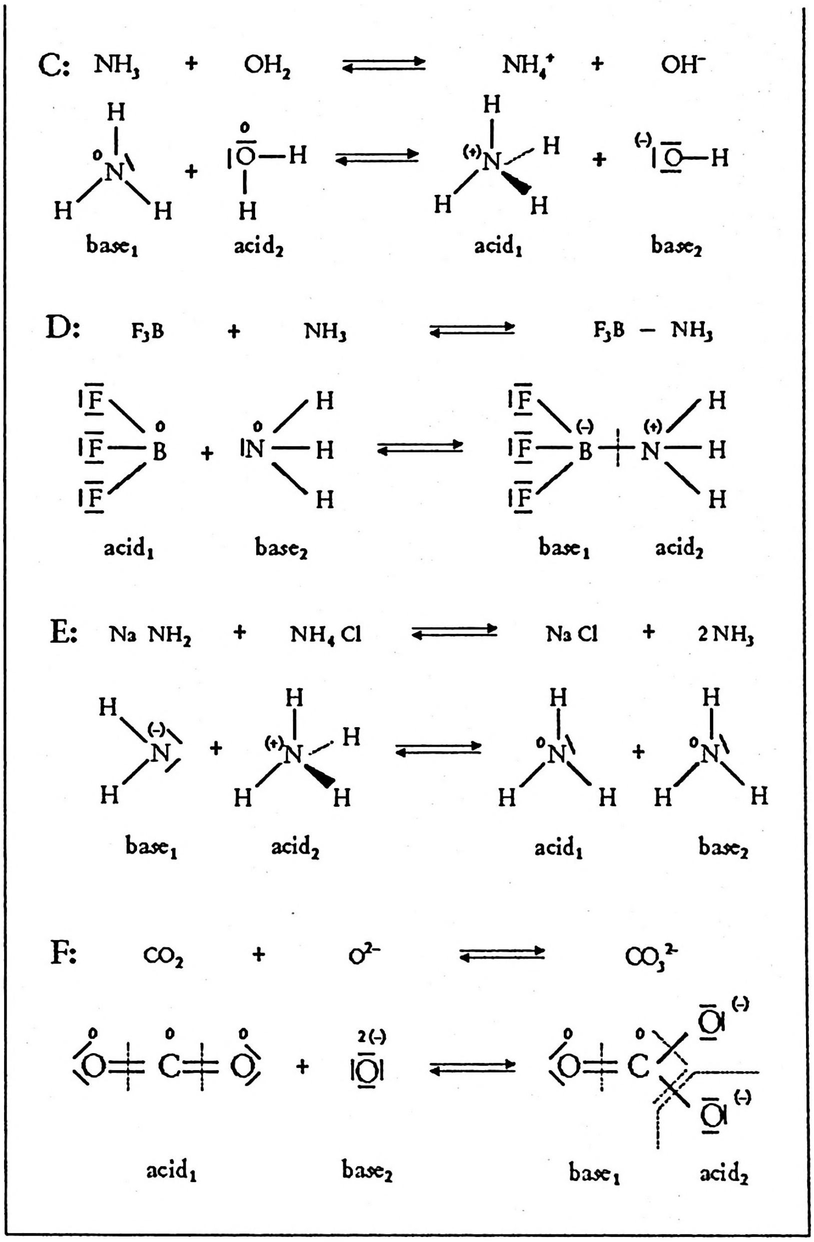


Fig. 4. *Six examples of acid-base reactions.*
Water is a reactant only in A, B and C. The electric charges assigned to the more representative atoms correspond to their formal charges. See also legend to fig. 1.

is the atomic group, atom or ion whose positive formal charge *decreases* (or increases if negative) without changing its oxidation number. The base is the atomic group, atom or ion whose positive formal charge *increases*.

All these examples indicate that this method to identify acids and bases encompasses the definitions of these chemical concepts given by Arrhenius, Bronsted, Lowry and also Lewis.

As a conclusion, it can be said that the strongest acid would be the proton (H^+) that does not exist in water solution because it immediately reacts with water to form a covalent bond losing its positive formal charge. The strongest base would be the O^{2-} ion of the alkaline or earth--alkaline oxides.

The reaction of carbon dioxide (acid) with calcium oxide (base) under anhydrous conditions is presented in fig. 4F. It clearly shows that CO_2 behaves as an acid because one of its oxygens gains a negative charge. The O^{2-} ion is the base because it loses one electron.

Finally, a comparison of the red-ox and acid-base concepts can be expressed as follows:

An oxidant gains electrons considering its molecular bonds as *ionic ones* and an acid gains electrons considering its molecular bonds as *covalent ones.*

A reductant and a base behave respectively in the opposite way.

We think that these definitions for acids and bases are very simple and clear, and they can be used as a universal criterion since they unify in a logical way the various definitions that are commonly used.

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Se estudian ejemplos clásicos de los procesos fisicoquímicos habituales llegando a una conclusión unificadora. En los procesos red-ox son oxidantes los átomos o grupos de átomos que ganan electrones de acuerdo con sus respectivos números de oxidación, es decir, si consideramos los enlaces como iónicos puros y en los procesos ácido-base son ácidos los átomos o grupos de átomos que solamente ganan electrones de acuerdo con su carga formal, es decir, si consideramos los enlaces como covalente puros.

Palabras clave: Ácido-base, red-ox, Electronegatividad, Número de oxidación, Carga formal.

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