Interactions Between a Condensed Target and a Non-Equilibrium Plasma: Acid-Base Reactions at the Interface

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Interactions Between a Condensed Target and a Non-Equilibrium Plasma: Acid-Base Reactions at the Interface

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A new approach of plasma processes of industrial use is presented, with emphasis on the chemical properties of the plasma gas. Reactions occurring at the gas/target interface are for the first time interpreted in terms of acid-base reactions and pertinent examples are given of laboratory experiments and of industrial treatments (e.g., etching, plasma polymerization or surface modification processes). Proton exchanges between the plasma phase and an aqueous target give evidence of Bronsted acid-base phenomena. Illustrations of Lewis acid-base characters are provided by the role of biradicals (e.g., halogenocarbenes, nitrene) which are the main reacting species in etching or in surface treatment processes.

Key words: Non-equilibrium Plasma; Gas Phase Acid-Base Reactions; Plasma phase acid-base reactions; Plasma surface interactions; Plasma Processes; Etching; Plasma Polymerization; Nitriding.

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Introduction

A number of the newest industrial techniques in the field of surface treatment, are connected to plasma processes. We plan first to recall briefly what is termed a chemical plasma and to examine from the chemist's point of view the particular properties of this (still) unusual medium which involves both ions and uncharged species such as radicals in their fundamental or excited state. Our approach will deliberately minimize energy transfers and cross sections which are familiar concepts to physicists. We will concentrate on the chemical aspect and consider the properties of a non-equilibrium plasma in terms of acid-base reactivity, which has not yet been done. This point of view needs first an outline of the acid-base classical concepts which will appear to chemists to be trivial; we will then illustrate them by selected examples taken in various fields of plasma treatments: the etching processes in microelectronics, which involve acid-base characters; the plasma polymerization processes in which radicals occur determinately; the surface modification of metals and catalysts.

At this juncture, it can be pointed out that reactions are much faster in the gas phase than in a condensed phase, also the value of the kinetic constant in a solvent depends strongly on its nature. For example, the reaction:

\[ \text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Cl} + \text{Br}^- \]

is more than $10^{10}$ times faster in the gas phase than in any classical solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>H$_2$O</th>
<th>CH$_3$OH</th>
<th>DMF</th>
<th>gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (cm$^3$ mol$^{-1}$s$^{-1}$)</td>
<td>$8.2 \times 10^{-27}$</td>
<td>$1.1 \times 10^{-26}$</td>
<td>$6.7 \times 10^{-22}$</td>
<td>$2.1 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

This is mainly due to solvation, which always occurs in a condensed phase but may not affect species in the gas phase.

Both duration of treatments and solvent occurrence are troublesome events in industrial processes; this is the reason why the industrial world is looking for dry processes for the most modern technologies.
The plasma phase: definitions and general characters

A plasma results from the interactions between electrons and gaseous matter and includes neutral and ionic species both in fundamental or excited states. The neutral species are molecules (and occasionally clustered molecules) and radicals, while charged species involve electrons, anions and cations. When the temperature of the electrons $T_e$ balances that of the gaseous particles $T_g$, we have a "hot" plasma for which the thermal equilibrium is reached. Otherwise, and for most of the cases, the temperature of the electrons is much higher: this "cold" plasma is usually realized in low-pressure luminescent discharges or in corona discharges (for which $p < 1$ atm) [Fig. 1] and will be considered in this paper.

The energy balance shows that $T_e$ and $T_g$ are correlated:

$$\frac{T_e - T_g}{T_e} = \frac{n m_e (\lambda_e \cdot e E)^2}{24 m_e (K T_e)^2} \quad [1]$$

with $m_g$ mass of heavy particles; $m_e$ mass of electrons; $\lambda_e$ mean free path length of the electrons; $E$ electric field strength; $n m_e E E$ amount of electron energy along one mean free path length; $K T_e$ average thermal energy of the electrons.

In the considered plasmas, energy is carried on by the electrons and depends on various parameters such as gas pressure, gas composition and diameter of the reactor. Von Engel (1955a) suggests a semi-empirical relation to get within an order of magnitude of $T_e$:

$$\left(\frac{eV_i}{K T_e}\right)^{-1/2} \times \exp \left(\frac{eV_i}{K T_e}\right) = 1.16 \times 10^7 \left[\text{CPV}\right]^2 \quad [2]$$

with $e$, electron charge (coulomb); $V_i$, ionization potential (e.g., Ar = 13.12 volts; Ne = 15.6 Volts); $T_e$, electron temperature (K); $r$, radius of the discharge reactor (cm); $C$, gas constant (e.g., He = 4.10^{-5}; H$_2$ = 10^{-5}; Ne = 6.10^{-5}; Ar = 4.10^{-5}; $P$, pressure (mm Hg); $K$, Boltzmann Constant.

Example for nitrogen:

<table>
<thead>
<tr>
<th>$P$ (torr)</th>
<th>$C$</th>
<th>$r$</th>
<th>$CPV$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4*10^{-2}</td>
<td>5</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>4*10^{-2}</td>
<td>1.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Energy is dissipated through collisions between electrons and particles: this governs the plasma composition as qualitatively sketched on Fig. 2. Besides, the energy distribution of the electrons obeys the Druyvesteyn law (von Engel 1955b):

$$f(e) = C e^{1/2} \cdot \exp \left( -0.55 \left(\frac{e}{\bar{e}}\right)^2 \right)$$

[3]

with $\bar{e}$ energy of the electrons; $\bar{e}$ average energy; $f(e)$ distribution function of the electrons.

Fig. 2. a-Sketch of energy dissipation between species in the plasma phase. Neutral species (molecules, radicals, photons) and charged species (ions and electrons) are formed. The heavy particles may be also found in an excited state.

b-Interaction of the heavy particles (in excited or ground state) with photons give rise to charged or uncharged radicals ($i^0$, $j^0$) excited or not. By electron rearrangement the charged radicals generate ions in excited or ground state (not shown). As ultimate matter balance, a plasma involves mainly neutral species (molecules $M$, radicals $i$) in excited or ground state, ions ($M^+$, $M^-$) in excited or ground state and electrons.

The intersection of $f(e)$ and the excitation cross section for a given molecule provides the population of an excited state [Figs. 3, 4, 5]. We are now in position to determine the main excited (vibrational and electronic) states in the discharges which are responsible for the energy transfers and for changes of the chemical properties: new electronic states; increase of electronic density on antibonding orbital leading to weak chemical bonds and increase of reactivity; orbitals reactivity; triplet states, i.e., radical productions; vacancy orbitals and free pair of electrons (Lewis acid-base properties); ion formation;
Plasma-Surface Interactions

We report in Fig. 6 the electronic structure of the methyl radical chosen as an example CH₃⁺, which results from a homolytic breaking of the CH₃ - H bonding if the discharge occurs in methane, can undergo combination reactions with other radicals H⁺ or CH₃⁺. In suitable conditions CH₃⁺ may also catch (or leave) an electron to give the corresponding anion radical CH₃⁻ (cation radical CH₃⁺⁺) which has the same number of external electrons as the methyl anion (methyl cation respectively), but the electron distribution is different. After rearrangement CH₃⁻ gives rise to the methyl anion, all the quantic boxes of which are filled [Fig. 6]. CH₃ may then share an electron pair with a convenient electron pair acceptor species. Similarly the methyl cation in the singlet excited state has a particular electron distribution characterized by an empty orbital, which can be filled by some electron pair given by an electron pair donor group.

A general survey of the shapes and properties of radicals occurring in plasma processes is given on Fig. 7 and in addition, the formation of biradicals has to be mentioned: as underlined by the example of the carbene :CH₂ [Fig. 6] (or the halogenocarbenes) these species may present one empty orbital in a singlet excited state.

One can point out that chemical reactions involving the plasma phase may occur in the plasma phase itself, e.g., O₂⁺(Δg) for the synthesis of O₃ or NO. The chemical reactions may also take place in the plasma/surface boundary layer and the relevant examples which are typical of plasma surface processes can be found in etching of silicon wafers or in plasma polymerization according to the main mechanism involved (respectively acid-base or radical mechanism).

Acid-base properties: general survey and definitions

Various aspects of the acid-base reactions

Acid-base phenomena are concerned with two typical processes according to the underlying definitions. The proton exchange processes between the acid AH and the associated base A⁻:

\[ AH = A^- + H^+ \]  [4]

are called Bronsted acidity (or basicity). The electron pair exchange between a donor species D (the base) and an acceptor molecule A (the acid) are called Lewis acidity (or basicity):

\[ A^- + D = AD \]  [5]

Molecules occurring in reactions of this kind present the following characters: acids are species with at least one empty orbital (e.g., BF₃), the positively charged end of a π bonding (e.g., O=C=O), positively charged ions, which are able to catch electrons; bases are species with a lone electron pair, anions (e.g. F⁻, O⁻), the negatively charged end of π bondings (e.g., >C=O⁻). The Lewis concepts for acidity or basicity thus defined display a more general character than Bronsted’s definitions and include the proton exchange phenomena.

The question of the quantification

Any equilibrium is usually determined by the relevant equilibrium constant K (or by the associated standard free energy ΔG°). For the proton exchange equilibria, H⁺ occurs in every reaction and therefore plays a prominent part. The strengths of the bases are thus referred to their ability to combine with H⁺.

In the gas phase, the concerned species are often unsolvated or bare; the acid-base character is then quantified by

negative ions (reduction properties); positive ions (oxidation properties); modification of the molecular shape; modification of the symmetry, bond angle, hybridation, loss of atom and radical formation; vibrational excitation.

Radical Production

The sketch of energy dissipation [Fig. 2] shows that the collisions between electrons and gaseous species may result in the formation of radicals, which may also come from the interactions of photons with molecules or ions.
either the gas basicity (GB) or the gas acidity (GA), which are defined in terms of standard free energies. For equations [6] and [7] in the gas phase:

\[
AH = A^- + H^+ \quad [6]
\]

\[
BH^+ = B + H^+ \quad [7]
\]

we have

\[
\Delta G^\circ_6 = GA(AH) \quad [8]
\]

\[\Delta G^\circ_7 = GB(B) \quad [9]\]

and we can consider

\[\Delta G^\circ_{6-} - \Delta F^\circ_6 \quad [10]\]

\[\Delta G^\circ_{7-} - \Delta F^\circ_7 \quad [11]\]

as a first approximation since the entropy terms remain little with respect to the enthalpy term \(\Delta S^\circ\) may however be calculated (Hartman et al. 1979) on the basis of statistical thermodynamics.

The standard enthalpies can be calculated in terms of proton, hydrogen or electron affinities (resp., \(PA, HA, EA\)) binding energies \(D\), ionization potentials \(IP\) by means of Haber cycles [Fig. 8]. Then:

\[
\Delta F^\circ_6 = PA(A') \quad [12]
\]

\[\Delta F^\circ_7 = PA(B) \quad [13]\]

\[GA(AH) \_ D(AH) + IP(H) - EA(A) \quad [14]\]

\[B(B') - HA(B') + IP(B) + IP(H) \quad [15]\]

The proton affinities of the basic species \(B\) or \(A^-\) provide a quantitative information on the basic character of the species.

**Acidity scales**

On the basis of a limited number of reference data, it is convenient to compare the acidity or basicity of various compounds. For this purpose we resort to the following equilibria [16], [17]:

\[
A_1 H + A_2^+ = A_2 H + A_1^- \quad [16]
\]

\[B_1 H^+ + B_2 = B_2 H^+ + B_1 \quad [17]\]

The use of suitable Haber cycles leads to:

\[\Delta F^\circ_{16} = [D(A_1 H) \_ EA(A_1)] - [D(A_2 H) \_ EA(A_2)] \quad [18]\]

\[\Delta F^\circ_{17} = PA(A') \_ PA(A') \quad [19]\]

\[\Delta F^\circ_{17} = PA(B) \_ PA(B') \quad [20]\]
The calculated $\Delta H^{\circ}_{16}$ or $\Delta H^{\circ}_{17}$ values allow then to build numerous ladders by measuring the displacement of equilibria [16] and [17] which involve some reference species. A number of published data (Hartman et al. 1979; Aue and Bowers 1979; Bartmess and McIver 1979; Berthelot and Gal 1984; McIver 1981; Arpino 1982) show that the PA values are generally included in a range of 1700 kJ mol$^{-1}$; most of the organic acids can be found in a 300 kJ area the upper limit of which is H$_2$O (723 kJ mol$^{-1}$) and in a similar way, the organic bases are in a 300 kJ range centered around NH$_3$ (GA = 860 kJ mol$^{-1}$) [Fig. 9].

As already mentioned the solvation phenomena which occur in a solvent phase deeply modify the reactivity of the species. They prevent the direct use in the gas phase of any classical acidity function relevant to a solvent phase, like the pH scale in water, without the previous determination of solvation numbers and solvation standard free energies.

**Applications**

The published PA values relevant to a given family of compounds have been used to verify correlations with structural data (Yamdagni et al. 1974; McMahon and Kebarle 1977) (e.g. Hammett's $\sigma$ or Taft's $\sigma^*$ parameters). Besides the "natural" order for the acidities in the gas phase has been recovered for various families of compounds (Yamdagni and Kebarle 1971; Davidson and Kebarle 1976; Arshadi and Kebarle 1970; Payzant et al. 1971) (alcohols, amines RNH$_2$, R$_1$R$_2$NH, R$_1$R$_2$R$_3$N, or even substituted acetic acids); the different order of the pK$\alpha$s is controlled by the stabilizing solvation effects on the charged species.

**Bronsted acid - base phenomena in the plasma phase**

**Bronsted acidity**

In the gas phase, the Bronsted acidity which is illustrated by the displacement of equilibria [6], [7] or [16], [17] has been examined by means of Ion Cyclotron Resonance, High Pressure Mass Spectrometry or various flow techniques (McIver 1981; Beauchamp 1971; Moylan and Brauman 1983).

In the plasma phase, no systematic investigation is available up to now, and this study was undertaken in our group, both to gather fundamental information and to explain a number of reactions occurring in the surface treatments (Amouroux et al. 1985a; Amouroux et al. 1985b) by means of plasma and to foresee new possibilities. We selected first aqueous solutions (Brisset and Amouroux 1985) of coloured acid-base indicators as the condensed phase since this target leads to more easy interpretations on the basis of Bronsted's concepts and a point-to-plane dc. corona discharge as the plasma source.

**Experimental device**

The general design of the 2-electrodes reactor is given in Fig. 10; particular details are displayed as follows: i) The gas inlet is made of a hollow needle, the active electrode; ii) The passive electrode is a stainless grid which acts as an ion collector; iii) The liquid target (cf. supra) laid on a microscope slide over or under the grid can be examined spectrophotometrically by means of two optical fibers connected respectively to a monochromator and a photomultiplier. The device allows us to follow the absorbance of the liquid slide at various wavelengths for various durations of the discharge [Fig 11].

Further developments of the reactor involve the use of a magnet and a modification of the axis of the active electrode.

**Results with a cylinder-like symmetry device**

When the active electrode set out was perpendicular to the grid, we obtained the following experimental results: whatever might be the nature of the gas (i.e. dry Ar, H$_2$O...
Fig. 10. -Diagrammatic view of the 2-electrodes reactor. 
[Typical working conditions: Plasma gas: Water saturated Argon; p = 1 atm.; flow rate = 0.3 liter/mn. Electric conditions: Distance between the two electrodes: 0.65 cm; Polarity: Rod +, grid - ; Voltage: 3 kV; Intensity: 200 µA. Target: Aqueous solution of Bromothymol Blue. a: Optical fiber and guide (from the monochromator); b: hollow needle for gas inlet and active electrode (to R= 25 MQ); c: plastic cap; d: glass reactor; e: stainless grid and metallic holder; f: microscope slide and liquid droplet; g: gas outlet; h: optical fiber and guide (to P.M.); i: Electrode (to generator).

Fig. 11. -Absorbance spectrum of an aqueous solution of Bromothymol blue and its evolution with the discharge duration; half life estd: 10 s.

Lewis acid-base phenomena in the plasma phase

Evidence of Bronsted acidity processes at the plasma/solution interface has just been reported: its systematic study is under development in our laboratory.

Lewis acid-base reactions may also occur in the plasma phase if the concerned species act as electron pair donors (bases) or acceptors (acids), that is if the distribution of their molecular orbitals are convenient. These species are atoms or molecules either in the fundamental or in some particular excited state.

As (more or less classical) examples of acids, we can mention boron trihalogenides BX₃ which are of common use in the etching processes:

:SO₂ + BF₃ → :SO₂BF₃

Except for iodine I₂ which "accepts" the base Γ, the halogens X₂ show generally no acid character (Cl₂ forms a complex with PCl₃, but its formation involves a structure modification and is more likely considered as an oxidative addition). IC₁₃ which is a saturated Ar, NH₃, CO₂): whatever be the position of the target with respect to the grid (target between or outside the electrodes); whatever be the polarity of the active electrode, the solution is always observed to become acidic as shown by numerous indicators.

The inter-electrode space can be divided into two areas; the first one in the immediate surroundings of the point is the ionization region and the second a diffusion or drift region. In a negative rod configuration, for example, cations, anions, electrons and neutral species can be found in the ionization region while only neutral and negative species exist in the drift region. In the positive configuration only cationic and neutral species exist in the drift region.

Our results show obviously that the acidic effects in the solution are not governed by the electrode polarity and thus depend exclusively on the neutral species of the drift region. The number of protons created in the solution depends on the duration of the discharge and their formation may result from the interaction between the neutral species in the plasma phase and the water vapour at the plasma/solution interface. This model is strongly backed up by the use of NH₃ gas which leads to similar observations and by preliminary experiments performed with gel-dispersed indicators, which give evidence of the prominent influence of water at the interface.

In a more general way the influence of a liquid phase (in particular that of non aqueous aprotic solvents) is under investigation to get information on the mechanism of proton generation in the liquid phase.

Asymmetric discharge

In a cylinder-like symmetry device the electric wind which drifts the neutral species and the electric field which affects the ionic species are colinear.

In the case of a negative active electrode - both neutral and anionic species are confined in two co-axial cones and the neutral species have chemical prominent effects; on lowering the symmetry - for instance by setting the active electrode non-perpendicular to the grid, the two cones have different axes and opposite chemical effects which can be then observed. Along the axis of the needle, acidic effects are observed while in the direction of the electric field (which remains perpendicular to the grid) the solution turns to be basic. Acidic and basic effects can then be characterized and separated. The separation is also improved by the use of a convenient magnetic field due to a magnet.
the properties of the polymers prepared electrochemically.

Organic polymerization processes. It has been pointed out that protection involve a polarization step in the general plasma polymerization, electrode modification, encapsulation or surface acids with the solid electrodes according to their polarization. and the modified species are then able to react as Lewis bases or electrode acting as the cathode (Lecayon et al. 1982). In the inner is responsible for the chimisorption step: the binding of the charged metal a Lewis acid-base reaction may take place which monomer (almost a carbene head) is close to the negatively coating of poly-acrylonitrile which is realized on the Fe or Ni performed in Acetonitrile solutions, such as the electrochemical polarizability has already been examined (Hancock et al. 1983).

The relationship between Lewis acid-base behaviour and acidic or basic character of the bonding according to its direction. electron densities of heavy molecules in the boundary layer and molecules, it affects the electron distribution and backs up the hence dipole formations. In the particular case of t bonding Polarizability is F acceptor according to the reaction:

$$SF_4 + R_2NF \rightarrow SF_5^- R_2N^+$$

(however, in the presence of SbCl$_5$, SCl$_4$ undergoes a chloride transfer to give SCl$_3$(SbCl$_5$). The interhalogen fluorides XF$_n$ (n = 1, 3, 5 for X = Cl, Br; n = 3, 5, 7, for X = I; e.g., CIF$_3^-$) act as Lewis acids toward the base F$^-$ and give anionic species by fixing F$^-$ (e.g., CIF$_3^-$) but in the presence of BF$_3$, AsF$_5$, SF$_6$ which are better F$^-$ acceptors, they form cationic species by losing F$^-$ (e.g., CIF$_2^+$).

$$\text{CIF}_3 + \text{SbF}_5 \rightarrow \text{SbF}_6^- \text{CIF}_3^+$$

XeO$_3$ reacts with KF to give XeO$_2$ F$^-$/K$^+$ and has an acid behaviour in spite of its lone unshared electron pair; Xenon fluorides acts as fluoride ion donors (e.g., XeF$_2$ in the presence of strong acceptors such as SbF$_5$).

The trivalent compounds of N, P, S afford many examples of Lewis donors. In addition, phosphines, amines and sulfides undergo oxidation reactions to form stable compounds, the phosphine and amine oxides and the sulfoxides. The reaction involving NF$_3$:

$$\text{NF}_3 + 1/2\text{O}_2 \rightarrow \text{F}_3\text{N} - \text{O}$$

in which the oxygen atom may be considered as acting like an acid, has been observed under the electric discharge. Xenon fluorides are classified as F$^-$ donors as well as CIF$_3$ (while Br F$_3$ is F$^-$ acceptor according to the reaction:

$$\text{CIF}_3 + \text{BrF}_3 \rightarrow \text{CIF}_2(\text{Br F}_4)$$

Polarizability The strong electric field created between the electrodes (i.e., $10^5$ to $10^7$ V cm$^{-1}$) interacts with the gaseous matter in the neighbourhood of the electrodes. It induces large changes of the electron densities of heavy molecules in the boundary layer and hence dipole formations. In the particular case of π bonding molecules, it affects the electron distribution and backs up the acidic or basic character of the bonding according to its direction. The relationship between Lewis acid-base behaviour and polarizability has already been examined (Hancock et al. 1983).

This is strongly supported by polymerization reactions performed in Acentonitril solutions, such as the electrochemical coating of poly-acrylonitrile which is realized on the Fe or Ni electrode acting as the cathode (Lécaon et al. 1982). In the inner Helmholtz layer where the positively polarized end of the monomer (almost a carbene head) is close to the negatively charged metal a Lewis acid-base reaction may take place which is responsible for the chinsorpcion step: the binding of the monomer to the metal.

In the gas phase similar mechanisms may be considered and the modified species are then able to react as Lewis bases or acids with the solid electrodes according to their polarization.

Numerous applications in the field of surface polymerization, electrode modification, encapsulation or surface protection involve a polarization step in the general plasma organic polymerization processes. It has been pointed out that the properties of the polymers prepared electrochemically

Plasma-Surface Interactions

![Diagram of plasma-surface interactions](image)

Applications to etching processes

The use of silicon, silicon derivatives, AsGa and other metals in micro electronic components has lead to a variety of elaborate etching processes which involve for most of them a plasma treatment (Fig. 14). We must first point out that both etching and sputtering processes consist in passing a chemical from the solid to the gas phase by means of ionic or molecular beams (Snowdon and Heiland 1985), so that it is enhanced by the formation of volatile species. It is the reason why fluorinated species are generally involved in Si etching processes (since it allows volatile species such as SF$_4$ to be formed) while halogen derivatives are preferred for metal etching. The working gas is usually selected for its ability to give F$^-$ or CF$_3^+$ ions, which are generated from mixtures of fluorocarbons (CF$_2$, CCl$_2$, C$_2$F$_2$, C$_2$F$_4$,...), halogenocarbons (CCl$_2$, CCl$_3$, F$_3$,...) or halogen derivatives (Cl$_2$, Br$_2$, SCl$_2$, SF$_6$, NF$_3$,...) in various compositions.

The etching speed of a given solid material provides information on the reactivity of the gas (or the gas mixture) toward the solid under plasma conditions. It has been shown (Flann 1981; Flann and Donnelly 1981) that the etching speed was directly dependent on the number of F atoms present in the gas phase; however if the production of F atoms was the governing parameter, the etching speed of a given substrate should be greatest with pure fluorine as the active gas. Since
basic compounds (like F\textsuperscript{2-}). These mere considerations may explain occurs in the etching process, and we can therefore consider it in other fluorine compounds, it is likely that some other mechanism experiments show that much higher speeds can be observed with (e.g. XeF\textsubscript{2}, CIF\textsubscript{3}, NF\textsubscript{3}, ...).

The SiO\textsubscript{2} or Si\textsubscript{3}N\textsubscript{4} etching is a much slower process than Si etching ; this may be related to the relative acidity of Si and SiO\textsubscript{2} (or SiN\textsubscript{3}) toward the attacking agents which are most often Si etching ; this may be related to the relative acidity of Si and terms of acid-base properties.

In plasmaless processes [Fig. 15], no ion is concerned, and we have only chemical reactions between neutral species. The low etching speed observed with CIF confirms that it is a poor F\textsuperscript{-} donor (because Cl\textsuperscript{+} links to a CIF molecule to form Cl\textsubscript{2}F\textsuperscript{+} which hinders its activity). CIF\textsubscript{3} is a weaker F\textsuperscript{-} donor than IF\textsubscript{5} or Br F\textsubscript{5}, while the most reactive species are actually XeF\textsubscript{2} or Br F\textsubscript{3}, which are known to be good F\textsuperscript{-} donors in the presence of strong F\textsuperscript{-} acceptors like Si.

However, it has been pointed out that the etching speed is largely enhanced by the presence of an ionic flow (e.g. Ar\textsuperscript{+}) or the excitation of the surface by a convenient laser beam. Authors also found that the desorption step of fluorinated species was the governing stage of the etching process.

In plasma etching processes, ions are associated to neutral species, a strong electric field and a photon flow; the conjugated action allows isotropic and anisotropic etching. The etching speed depends on the electric field and increases with the electric power ; this may be connected with the polarizability of the gaseous molecules, the reactivity of which is affected by \textsuperscript{1}E\textsubscript{1}. Anisotropic etching is governed by the influence of the electric field which affects both ionic and polarized species; for example NF\textsubscript{3}, CIF\textsubscript{3} or XeF\textsubscript{2} allows one to reach etching speeds as high as 80,000 Å mn\textsuperscript{-1} under these conditions.

The electrode polarization is also a determining parameter as illustrated by the following sketch built on the order of the etching speeds.

Cathodic polarization ; Lewis acids : CF\textsubscript{2}\textsuperscript{+} < CF\textsuperscript{+} < CBrF\textsubscript{3} < BF\textsubscript{3}

Anodic polarization ; Lewis bases : CF\textsubscript{2}\textsuperscript{-} < CIF\textsubscript{3} < CIF\textsubscript{5} < SF\textsubscript{4}\textsuperscript{-}

The speed depends also on the gas pressure and temperature, but the main parameter is the gas composition. For example the etching speed of Si by NF\textsubscript{3} in NF\textsubscript{3} + He mixtures is higher than 10,000 Å/mn for 80 % NF\textsubscript{3} (i.e. more than five times the relevant value for 10 % NF\textsubscript{3} i.e., 2,000 Å /mn). In a similar way the etching speed of AsGa by Cl\textsubscript{2} + Br\textsubscript{2} mixture increases with the percentage in Br\textsubscript{2} (20 - 80 µm mn\textsuperscript{-1}). In that case, two different chemicals, As and Ga, are concerned, and the etching speed is an average value depending on the etching speeds of each pure component. Besides, the desired electronic properties of the material need the same etching speed be realized for both species. Occasionally the etching speed may not be a mere increasing function of the gaseous mixture composition (Flamm 1981; Flamm 1985), as emphasized by the Si etching by CF\textsubscript{4} + O\textsubscript{2} mixtures. In this case, the speed presents a maximum for a particular mixture close to 40 % CF\textsubscript{4}. This feature may be related
to the thermodynamic study of the gas mixture and sketched as
follows: oxygen allows carbon oxides to be formed which result
from the breaking of C-F bondings while fluorine attacks at Si to
form volatile fluorinated species. In SiO₂ etching, no oxygen is
needed in the working gas since the element is present in the solid
phase; the formation of CO and fluoro compounds (e.g. SiF₂, SiF₄,
SiOF₂) has been reported at the gas solid interface.

Polymerization process

The plasma polymerization is controlled by different
activation mechanisms such as ionic mechanisms, radical or
photonic activation. However, in a plasma reactor the three
phenomena generally occur and produce nonconventional
polymers which are in most cases highly crosslinked and adhere
to the solid surface. Nevertheless, we have to consider the
degradation phenomena due to the plasma-polymer interactions.

On the other hand the polymerization phenomena
depend on the nature of the substrate and we can consider the
different interactions between radicals or ions with the substrate:
- Interaction between the substrate and the radicals
  - non-volatile species formation ----> grafting; volatile
    species formation ----> etching, ablation.
- No interaction between the substrate and the radicals and/or
  the ions; deposition phenomena.
- Interaction between the lattice of the substrate and the
  radicals; diffusion, doping.

Because the ionization of the gas or the vapor involves
many highly energetic species on one hand, and the formation of
the free radicals due to the fragmentation of organic compounds
(monomers) in plasma on the other hand, it is difficult to
distinguish clearly between atomic (plasma-state) or molecular
(plasma-induced) polymerization (Yasuda and Hsu 1977).

The next scheme represents the plasma polymerization
mechanisms proposed by Yasuda.

---

Finally, general properties of gaseous mixtures can be
easily transposed to plasma reactivity such as acid base
properties.

Fluorocarbon polymerization on different targets

Fluorocarbon polymerization of monomers such as C₂H₂F₂
on different raw materials (silicon, glass, PET or pp) can be
developed by corona discharge or glow discharge plasma
(Amouroux et al. 1983a; Amouroux et al. 1985a; Amouroux et al.
1985b).

By using a tubular glow discharge reactor with an
inductive RF plasma, the plasma deposition on a silicon target
depends on the pressure and the power of the plasma. ESCA
analysis of the polymer (i.e., film formed on silicon) shows the
main chemical bonds present through a thickness of 100 Å of the
layer [Fig. 16]. The presence of CF, CF₂, C₂F and SiF or F⁻
functions depend on the plasma conditions and are in agreement
with the thermodynamic calculations [Fig. 17].

---

A decrease of the H/F and the C/F ratios of the gas
mixture induces etching mechanisms of the target while an
increase of these ratios allows a polymerization layer formation.

Taking the same monomer but employing another mode of
electrical excitation (high voltage corona discharge) provides
polymeric films grafted or deposited to the surface of a substrate
such as PET film [Fig. 18].

Role of the oxygen contamination during a fluorocarbon plasma
polymerization process

Oxygen molecules which are present in the plasma
reactor interfere in the different steps of the graft
polymerization. In the presence of O₂:

1 - during activation:
   plasma
   RH ----> oxidation + weak concentration
   Ar + O₂ of free radicals.

2 - after activation step:
   plasma
   RH ----> R° ----> R₀ ² peroxy radicals
   Ar (not very reactive)

---

It is interesting to note that the electrical field strength
in the boundary layer induces dipole-dipole formation and large
modifications of the electronic density. The electrical field also
influences the ionic polymerization as well as the orientation of
the polymers formed.
The first two reactions decrease the efficiency of the graft polymerization by destroying the carbon free radicals and the last reaction decreases the formation of fluoropolymers in the plasma.

By using ESCA and ESR analysis (Figs. 19-20) we have clearly demonstrated the competitive phenomena occurring during the deposition in the case of the copolymerization in a mixture of Ar + C₂H₂F₂ (15 % C₂H₂F₂ + 85 % Ar) onto the polypropylene (Rouzbeh, 1985; Rouzbeh et al., 1986). The study of the 1s portion of a typical ESCA spectrum of the treated PP in the different gas compositions indicated that the structure of the polymeric film obtained depends directly on the oxygen residual in the plasma reactor.

In order to eliminate the short length oligomers and the nonfixed homopolymers the treated PP films are washed with water (Fig. 20 - II) and acetone, (Fig. 20 - III) respectively. We have pointed out that when oxygen is excluded from the reactor the high stability of the layer obtained is measured by only a slight decrease of F/C ratio when washed with acetone; while the oxygen/argon/C₂H₂F₂ mixture produces fluorocarbon oxide groups which are rapidly eliminated upon water or acetone washing.

Role of the target

By using glass or metallic targets plasma polymerization would depend on the reactivity of fluorocarbon radicals with the atoms of the lattice. For example, in the case of a glass substrate, large diffusion of the fluorine atoms in the lattice through a depth of 0.2 to 0.3 µm indicates the chemical affinity of the target.
Conclusion of our study by means of ESCA, ESR and Complex equilibria.

The results obtained in our study by means of ESCA, ESR, complex thermodynamic equilibria, are coherent and show the important role played by the free radicals on the polymerization process.

The concentration and the nature of the free radicals depend directly on the interaction of the parasite radicals such as O₂ (p²) with the free radicals formed in the plasma. This reaction destroys the reactive species present in the gas phase by forming gas products which are not polymerizable (byproducts) as well as by destroying the carbon free radicals formed on the substrate (Fisher and Hellwage, 1962).

The ions and the electrons contribute as a whole to the development of the materials which are characterized by the space charges resulting from the discharge. Their stability in the time depends on the conductivity of the material and/or the inclusion of metallic atoms.

**Role of NH radicals in nitriding process.**

The comparative study of transition metals nitriding by various inductive (40 MHz, 1 kW), low pressure (5 mbars) plasmas : N₂, N₂ + H₂, NH₃ points out the role of NH radicals (Gicquel et al. 1983).

The presence of a lone pair in the external πₓ bonding orbital of the first electronic excited state confers to the NH radical its basic properties. The proton affinities of the N₂, N₂⁺, H⁺, NH₃, NH₂ and NH species, in their ground state, are given in table 1 ; the NH radical has therefore the highest basicity.

After 1.5 h of N₂, N₂ + H₂ or NH₃ plasmas action, the transition metal target reveals the formation, on its surface, of a

<table>
<thead>
<tr>
<th>Molecule</th>
<th>PA (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>522.5</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>522.5</td>
</tr>
<tr>
<td>NH₃</td>
<td>911.2</td>
</tr>
<tr>
<td>NH₂</td>
<td>1672</td>
</tr>
<tr>
<td>NH</td>
<td>&gt;1672</td>
</tr>
</tbody>
</table>

Table 1: Proton affinities
nitride layer (Gicquel et al. 1985a; Gicquel et al. 1985b). The ESCA and microhardness analysis of the metals make possible the determination of the nature and the thickness of the nitrided layer.

During the nitriding process, spectroscopic analysis of the plasma (Ricard, 1983) gives the emission intensity of the NH radical (A^3\pi\rightarrow X^3\Sigma^-) along the reactor and in the boundary layer at the plasma/target interface (D’Agostino et al. 1981).

Moreover, the vibrational temperature of N_2 (C^3\nu_1) gives a measurement of the excitation level of the reactive species (Amouroux et al. 1983b; Polanyi and Wong 1969). Taking as an example the tungsten nitriding; we observe the formation of a nitride WN after an ammonia plasma treatment while the formation of W_2N is produced after a N_2 - H_2 or a N_2 plasma treatment (Table 2).

Table 2. ESCA Analysis Results.

<table>
<thead>
<tr>
<th>Gas</th>
<th>W_4 H_2</th>
<th>N_2 H_2</th>
<th>N_2 W (50-50%)</th>
<th>W_2 N (20%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH_3</td>
<td>244.3</td>
<td>247.8</td>
<td>247.3</td>
<td>246.7</td>
</tr>
<tr>
<td>NH_3</td>
<td>396.7</td>
<td>396.2</td>
<td>396.5</td>
<td>396.6</td>
</tr>
<tr>
<td>% W</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10%</td>
</tr>
<tr>
<td>% WN</td>
<td>80%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>% W_2 N</td>
<td>20%</td>
<td>100%</td>
<td>100%</td>
<td>90%</td>
</tr>
</tbody>
</table>

The thickness of the nitried layer depends on the nature of the reactive gas, it varies as a function of the NH radicals density in the reactor (Fig. 22): it is maximum for a NH_3 treatment and minimum for a N_2 treatment. We can notice that in the N_2 - H_2 plasmas, the thickness of the layer increases as the percentage of H_2 decreases (Fig. 23), simultaneously the NH emission intensity and the N_2 vibrational temperature rise (Fig. 24).

The thickness of the nitrided layer depends on the nature of the reactive gas, it varies as a function of the NH radicals density in the reactor [Fig. 22]: it is maximum for a NH_3 treatment and minimum for a N_2 treatment. We can notice that in

Fig. 22. -NH emission intensity as a function of H_2 content in a N_2-H_2 plasma (input power: 1kW; pressure: 5 mbar; flow rate: 0.3 l/min).

Fig. 23. -Vickers microhardness versus diamond penetration depth for different plasmas (NH_3; 80% N_2, 20% H_2; 50%, N_2; 50% H_2) (input power: 1 kW; pressure: 5 mbar; flow rate: 0.3 l/min).

These results lead to the conclusion that a low hydrogen flow rate in the N_2 - H_2 mixtures controls the formation of the NH radicals. The nature of the nitride and the thickness of the layer depend on the flow of NH radical produced. The second example deals with the nitriding of titanium by a NH_3 plasma under pressures varying from 2 to 40 mbars. The microhardness measurements indicate that the thickness of the nitrided layer increases as pressure decreases or as input power increases. NH_3 decomposition rate (G.C. analysis) increases from 20 % to 80 % as pressure decreases from 13 to 1 mbar [Fig. 25]; correlative, the profiles of NH emission intensity measured
Plasma-Surface Interactions

Fig. 24. -Vibrational temperature of N₂ (C₃πₗ): \( T_v(N₂) \); rotational temperatures of N₂ (C₃πₗ) and of NH (A₂π): \( T_R(N₂) \) and \( T_R(NH) \) variations as a function of H₂ content in the N₂-H₂ plasma in presence of tungsten. (input power: 1kW; pressure: 5 mbars; flow rate: 0.6 l/min).

Fig. 25. -Variation of NH₃ decomposition rate, in the presence of titanium, as a function of pressure at constant residence time (20 ms) and constant input power (1.1 kW) (Ti-coil distance = 15.3 cm).

Finally, the vibrational temperature varies from 3000 K at 20 mbars to 3700 K at 2 mbars [Fig. 27]. The ESCA analysis reveals that the treated titanium target presents two Ti 2P₃/₂ photo electron peaks at 455 eV (TiN) and at 458 eV (Ti₂O₃N). The ratio of the relevant intensities increases with the thickness of the nitride layer (measured by microhardness) that means as the pressure decreases [Figs. 28, 29] (Table 3).

Therefore, there is a correlation between the evolution of the gaseous phase (reaction rate, NH emission intensity) and the evolution of the titanium surface (nature and thickness of the nitride).

As a conclusion, the nitriding process of transition metals, with an acid character due to the \( d \) orbitals, is determined by proton affinity of the species in the plasma phase, by the NH flow and by the vibrational excitation of the reactive species in the boundary layer (Purvis et al. 1979).
Fig. 28 - Treated titanium superficial Vickers microhardness for 25 g load as a function of pressure and input power. (flow rate: 0.31/min).

Fig. 29 - Deconvolution of the Ti 2p spectrum for P = 40 mbar and P = 2 mbar NH3 treatments. (input power: 1 kW; flow rate: 0.31/min).

**Table 3. Microhardness Measurements**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Input power: 1040 W-Time: 1 h30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mbars)</td>
<td>5</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>7</td>
</tr>
</tbody>
</table>

**Conclusions**

In this work we attempted to focus the attention on the acid-base phenomena in the plasma phase and we selected three typical examples in addition to demonstrative experiments: etching of microelectronic components, polymerization and nitriding processes. The basic concepts are derived from those developed in the gas phase. We have also to consider the influence of the charged species (ions and electrons), that of the electric field close to the electrodes which acts on the polarization of the species, and the presence of radicals and molecules in various excited states (especially the singlet or triplet states). All these species may undergo reactions and explain in part the observed kinetic mechanisms.

**Acknowledgements**

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**References**


Discussion with Reviewer

C. Boiziau: How do you explain that the etching speed is enhanced by ion bombardment or laser irradiation? What is the main parameter: the energy of the incident particle (ion or photon) or the beam intensity?

Authors: Reactions occurring at a solid surface (e.g. etching) usually involve 5 steps: i) the diffusion of the reacting species in the gas boundary layer, ii) the adsorption of the resulting species at the surface, on activated sites, iii) the chemical reaction between the adsorbed species and the substrate molecules, iv) the desorption of the reaction products from the surface, and v) the diffusion of the products through the boundary layer. Ions and photons act on the chemical reaction steps (i.e. steps ii) to iv) :

- the beam intensity is the major parameter for increasing the number of excited sites, and hence affects step ii.
- by contrast, ions and/or photons bring the species to an activated energy level and allow the reaction to take place (step iii). They also bring the products to an activated desorption process (step iv). Both steps depend on the energy carried by the particle.
- it is widely accepted that desorption occurs as a limiting step for surface reactions, and hence the overall kinetic mechanism is controlled by the desorption step. Therefore the main parameter is the energy of the incident particle (ion or photon).

C. Boiziau: It was demonstrated that the electrode polarization plays an important role in the electropolymorization processes (Boiziau and Lécayon 1986). For example the anodic polarization leads the metal surface to behave as a strong Lewis acid, which permits a large probability for acid-base reactions between metal and polarized molecules. You observe the same phenomena in the plasma etching and in the plasma polymerization processes, but you don't point out an eventual effect of anodic polarization in the nitriding process of transition metals- Why?

Authors: An etching reaction may be performed by gaseous ions of both signs which react with the substrate and act then as acids or bases. The plasma gases selected for polymerization and for etching processes are usually aliphatic halogen compounds (e.g., CF₃, NF₃, CH₂F₂, CO₂F₂, ...) which are used as single gases or as gaseous mixtures. Due to their electrophilic character these chemicals give rise more easily to anionic (e.g., CF₃⁻, F⁻, ...) than to cationic species: that means that the prominent etching reaction involves the base (the anions in the gas phase) and the substrate acting as a Lewis acid. In addition, an anodic polarization also favors the formation of anionic species which enhance the effect and is thus of classical use in etching and polymerization processes.

Nitrizing processes may occur according to two different ways.

On one hand the reaction path is characterized by a dissociative adsorption mechanism and concerns the neutral species: N₂⁺, NH, NH₂, NH₃ react at the target according to classical mechanisms (adsorption/reaction /diffusion). The substrate polarization favors the grafting of polar species (i.e. NH, NH₂, NH₃). Then, the reaction can be considered as an example of acid-base reaction between species in the gas phase and the substrate.

On the other hand, ionic species are concerned and lead to cathodic bombardment or sputtering processes according to the kinetic energy of the acting ions.

The low energy (10-20 eV) reacting species such as N₂⁺, NH⁺, NH₂⁺ are implanted in the negatively charged metal according to a cathodic bombardment process.

The high energy ions which are usually cations of 50-100 eV are accelerated through the cathodic sheath. The sputtering of the target then gives rise to metal clusters in the gas phase. The reaction between the nitrogen plasma and the clusters generates new nitride species which are usually redeposited on the target or on another polarized substrate.

V. Young: It has been indicated that ¹⁸O₂ state of O₂ behaves as a Lewis acid, and yet it is evident from Fig 12 that both ends of oxygen become involved in bond formation. It seems to me that O₂ (¹⁸O₂) should be regarded as an amphoteric substance, because it has both an empty quantic box and a quantic box containing a lone pair which probably don't differ much in energy. Why is O₂ (¹⁸O₂) considered to be a Lewis acid?

Authors: This question is right in the axis of our approach, and in addition gives evidence of our limited knowledge of the chemical properties of species in an excited state.

A number of compounds called "ampholytes" show both acid and basic behaviours with respect to the Bronsted criteria. Examples in water are HCO₃⁻ (the acid associated to CO₂⁻ and the base conjugated to H₂CO₃), the zwitterion forms of amino acids or even some oxides. This character may be of large occurrence in spite of the difficulty to find the conjugated form in the proper solvent. For example the protonation of amines (or anilines) is easy in "classical" solvents but the deprotonation which generates the amide ion RNH⁻ requires the use of highly basic media.

A similar approach could be formally applied to Lewis acid-base criteria although it would be rather unusual. We have to remember that oxidation and reduction can be considered as degenerated situations with respect to Lewis donor-acceptor criteria. In the following distribution of LUMOs and HOMOs of compounds A, B, C, D compared to M, A is oxidized, M reduced; B acts as the base and M as the acid; C is the acid and M the base; D is reduced and M oxidized. The question then is to select illustrations of these situations where M is the dioxygen, to complete the following examples relevant to O atoms. In numerous molecules the O atoms are donor centers, but in a limited number of situations O can be considered as a Lewis acid. Textbook examples are related to oxide formation:

R₃N/X₃P /R₂S /R₂SO O atom transfer...
O₂ is easily reduced into the oxide ion O₂⁻ which is of wide occurrence, so that the A/M system is illustrated by paramount examples. The oxidation of dioxygen occurs in the formation of O₂F₂ from O₂ and F₂ in a glow discharge (D/M system). Examples of C/M systems are provided by oxygen adsorption onto metals which act as Lewis acids.

Before we review the most typical reactions involving dioxygen as a ligand we have to come back briefly to the mechanism itself. We will limit it to the electrophilic reactions and keep in mind that this label refers to reactions provoked by electron poor species (e.g., H⁺, Lewis acids with their empty quantic box) which first attack at electron rich molecules (e.g., olefins, Lewis bases). The mechanism follows then two ways which result in an addition or a substitution.

Dioxygen gives adducts with molecules called "oxygen carriers" which are usually transition metal complexes. The fixation of O₂ takes place at the metal center. Recent studies suggest an angular superoxo structure M-O-O and arguments are given in favour of "oxidative addition" for several compounds. Examples are also reported of peroxo structures characterized by bondings between the metal center and both ends of the dioxygen molecule. A matching example is the famous Vasca's complex, Ir₁Cl(CO)(Ph₃P)₂ which has been thoroughly studied; its structure has been examined in terms of occurrence of small molecules in an activated state. This point of view has been discussed by Vasca himself but it is backed up by some classical mechanisms which characterize O₂(¹Σg) occurrence.

The most important chemical reactions which are specific to singlet oxygen concern alcenes, dienes or aromatic compounds, and also some heterocycles. In addition particular reactions take place with amines, phenols or sulfides. Most of the relevant examples illustrate the electrophilic character of O₂(¹Σg); the details of the mechanisms are however still under consideration:

i) The cycloaddition of singlet oxygen at an activated double bond leads to the formation of 1,2 dioxethanes. These compounds of generally poor stability give rise to a couple of carbonyls (one of them is in an excited state):

ii) The "ene" reaction refers to the addition of O₂ on alcenes with a labile hydrogen in the 3 position. It leads to the following hydroperoxides

iii) The 1,4 cycloaddition (Diels-Adler type) gives endoperoxides

These reactions may be compared to those previously quoted of the oxygen carriers or those of singlet oxygen quenchers which are usually polyethylenic molecules.

iv) We also mentioned various reactions of O₂(¹Σg), for example with amines, phenols and sulfides, but except for the last case the relevant mechanisms are different and do not involve the electrophilic character of singlet oxygen. Even for the reaction with sulfides

\[ R₂S + O₂ → [RSO₂] → R₂S + 2R₂SO \]

the mechanism and the structure of the intermediate are still under discussion.

**Authors:** A few decades ago, a classical use in solution chemistry was to consider the acidity and basicity constants which appeared as direct consequences of Arrhenius's (1887) or Usanovich's (1939) definitions for acidity and basicity.

When an acid or a base is dissolved in water, an hydrolysis reaction takes place:

\[ \text{Acid} + H₂O = \text{Base} + H_3O⁺ \]  
\[ \text{Base} + H₂O = \text{Acid} + OH⁻ \]  

Both equilibria (1) and (2) are equivalent to each other since we have:

\[ Ka•Kb = Kw. \]

The strength of the acid/base system is defined by any constant \( K_a \) or \( K_b \):

\[ K_a = (\text{Base}⁺)(\text{H}_3\text{O}⁺)/(\text{Acid}) \]
\[ K_b = (\text{Acid}⁺)(\text{OH}⁻)/(\text{Base}) \]

with \( K_a*K_b = K_w \). Let us consider the example of an aqueous solution of ammonia:

\[ \text{NH}_3 + H₂O \rightarrow \text{NH}_4OH = \text{NH}_4⁺ + \text{OH}⁻ \]
\[ \text{NH}_4⁺ + H₂O = \text{NH}_3 + H_3O⁺ \]

We verify that \( K_a*K_b = K_w \). In order to simplify, only one constant is now used, and we keep the acidity constant \( K_a \).

When people became interested in gas acidity or gas basicity, the same historic way was likely followed and it was found clearer to keep the symmetry between H⁺ and OH⁻. In fact only one parameter is needed provided the acid/ base system considered be unambiguously defined. The proton affinity PA appears now to be the most popular parameter to characterize an acid/base system. The strongly basic species are associated to high PA values; since GB varies in the same way as PA, the strong bases are related to high GB values. For example, the 1-Me-2,6-t-butylpiperidine (PA= 1001 kJ/mol; GB = 968 kJ/mol) is among the strongest bases known in the gas phase.
The protonated form associated to a strong base is a very weak acid, as easily guessed from classical considerations. We demonstrate in the paper that the strength of an acid can be estimated by means of the GA parameter: the high GA values are relevant to very weak acids and the low GA values to the rather strong acids.

A given acid/base system involving the acid and the conjugated base can be characterized by a unique parameter, the GA of the acid or the GB of the base (or as well the PA of the base). These parameters are equivalent since the use of GA(acid) or GB(base) is unambiguous. Besides, they take the same numerical value, and we have for the example of the ammonia system

$$\text{GA}(\text{NH}_4^+) = \text{GB}(\text{NH}_3).$$

The piperidine derivative previously mentioned is a stronger base than ammonia, and its associated acid is a weaker acid than $\text{NH}_4^+$. Then we have:

$$\text{GB}(\text{Pi}) > \text{GB}(\text{NH}_3) \quad \text{PA}(\text{Pi}) > \text{PA}(\text{NH}_3)$$

$$\text{GA}(\text{PiH}^+) > \text{GA}(\text{NH}_4^+)$$

with also $$\text{GA}(\text{PiH}^+) = \text{GB}(\text{Pi}).$$

In other words, the lower GA values correspond to the stronger acids while the higher GB values are related to the stronger bases. The direction of the GA variations with the strength of the acids is rather disturbing to our mental schemes; one may find here the reason why GB, or PA, is presently preferred to GA as the characteristic parameter of a given acid/base system.