

Reading fitness landscape diagrams through HSAB concepts



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ABSTRACT

Fitness landscapes are conceived as range of mountains, with local peaks and valleys. In terms of potential, such topographic variations indicate places of local instability or stability. The chemical potential, or electronegativity, its value changed of sign, carries similar information. In addition to chemical descriptors defined through hard-soft acid-base (HSAB) concepts and computed through density functional theory (DFT), the principles that rule chemical reactions allow the design of such landscape diagrams. The simplest diagram uses electrophilicity and hardness as coordinates. It allows examining the influence of maximum hardness or minimum electrophilicity principles. A third dimension is introduced within such a diagram by mapping the topography of electronegativity, polarizability or charge exchange. Introducing charge exchange during chemical reactions, or mapping a third parameter (f.i. polarizability) reinforces the information carried by a simple binary diagram. Examples of such diagrams are provided, using data from Earth Sciences, simple oxides or ligands.

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1. Introduction

Chemistry is actually a major component of the economic industry that helps in discovering or designing new molecules that take more and more place into our common life. This has been possible through the understanding of chemical reactions, through descriptors that rule the attracting power of elements. It constitutes the basis of the well established hard-soft acid-base (HSAB) concepts [1]. Later on, density functional theory (DFT) formalized and allowed quantification of such concepts [2], providing tools for understanding complex structures and properties of ions, simple elements, molecules or complex compounds.

In the case of usual chemical reactions, such concepts present a restricted interest for binary reactions since results are more or less predictable. For complex molecules, they determine which sites offer the most favorable place to add elements through chemical reactions. In case of very complex reactions, like it is the case in geochemistry or biochemistry, the number of reactive elements is too large to predict a reaction. For instance, natural rock systems deal with a dozen of elements in variable proportions. Such systems naturally evolve and trends have long been recognized between elements [3]. For instance, in silicate melts, a binary plot indicates iron oxides variation vs. SiO₂ increase (Fig. 1). Fractional crystallization and chemical differentiation provide a posteriori explanations to such trends. Indeed, the progressive incorporation

of ferro-magnesian elements in biotite and muscovite with decreasing temperature explains the observed trend. Calibration in temperature can be added to the diagram (Fig. 1), assuming a range of breakdown temperature for ferro-magnesian minerals. Nevertheless, it does not provide the chemical explanations for such trends. It explains how, but does not answer why such reactions develop.

Simple tools using HSAB and DFT concepts are suggested to give new insights to reactions, elements attraction, and charge exchange along reaction paths. Such tools are constructed assuming two- or three-dimensional (2D,3D) diagrams. They are designed from the chemical descriptors issued from the HSAB concepts [4]. The diagrams are essentially qualitative, but they help understanding a posteriori why elements combine together. Conversely they may help in determining to which elements or group of elements they could find affinity compared to other elements. Combining chemical descriptors incorporates also the major principles ruling chemical reactivity, as well as the charge and energy exchange during reactions. They illustrate trends when elements combine together, the most probable chemical paths being ruled by the major principles of maximization or minimization [5]. Such illustrations of chemical reactions are non predictive, but they allow discriminating between chemical paths, suggesting those that fit more within the principles.

The present paper is organized as follows. It first introduces the chemical descriptors from HSAB concepts and computed from DFT. They give place to evolutionary trends toward maximum/minimum principles, as determined from theoretical ground. Examples of fitness diagrams are provided, starting from a simple

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binary diagram on which the principles are superimposed. Further on, a 3D diagram shows the topography of a descriptor, with valleys and mountains, i.e. regions of stability and instability, according to the principles. A final possibility investigates the path of chemical reactions within such diagrams, suggesting the preferential paths in terms of energy exchange, or stability regions in which reactions should preferentially develop.

2. Chemical descriptors

Under HSAB concepts, quantified by DFT [2,4,5], four major parameters determine the potential reactivity of an element. Electronegativity (χ) is the chemical potential (μ), with a sign changed. It determines the power to attract an electron, since it corresponds to the first derivative of the energy when an electron is added or removed for the element, whereas the other variables (pressure, temperature) are kept constant. Hardness (η) is the second derivative of the energy in the same conditions. It indicates the resistance to a charge transfer. A third parameter, electrophilicity ($\omega = 0.5 \chi^2/\eta$) combines the two preceding ones [6]. It indicates the deficiency in electrons of an element. Considering the geometry of the energy surface, χ would be the equivalent of a tangent plane, and η would be the analogue to the radius of curvature. In a dynamic analogy, χ would be analogue to the velocity and η to the acceleration as the first and second derivative of motion. Under those assumptions, ω could be regarded as the twist, i.e. the normal component of the acceleration, tending to deviate the curve off the plane of motion. A fourth quantity, polarizability (α) indicates the tendency of an electron cloud to be distorted from its normal shape when in presence of an external electronic charge [7]. It is linked to electronegativity [8]. Negative ions have excess electrons and a large ionic radius, which make them highly polarizable. Conversely, the electronic cloud of small highly charged cations, such as most common metals, can easily distort under the influence of an external field. The maximum charge exchanged during reactions is limited by the quantity $N = \chi/\eta$ [9] easily transformed in values of ω/η . Simple principles state that reactions should evolve toward maximum hardness (MHP), toward minimum electrophilicity (mEP) or toward minimum polarizability (mPP) [5]. Reactions should also take place exchanging a minimum energy. Combining those four parameters and the four principles provide useful insights on chemical reactions.

The chemical reactivity values can be measured experimentally [10] or theoretically computed for simple species using DFT [11]

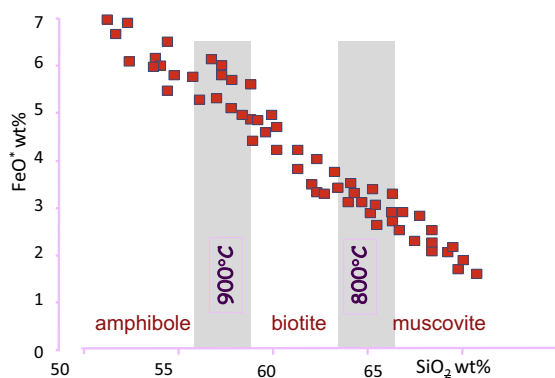


Fig. 1. Binary diagram displaying the variation in iron oxide ($\text{FeO}^* = \text{FeO} + \text{Fe}_2\text{O}_3$) as a function of silica content, both in wt%, in a standard felsic rock. The diagram can be roughly calibrated in temperature according to the successive breakdown of muscovite, biotite and amphibole. However, the diagram does not provide information on the source region and/or evolution of the melt, except the decrease in Fe-oxide with SiO_2 .

through a standard Gaussian code B3LYP/6-311 + G(d) [12]. The extension of those values to complex solutions uses geometrical averaging, based on the equivalent chemical potential [13]. Such sets of parameters and principles are efficient in indicating how elements and molecules should combine together. A combined use of those parameters would help in a better understanding of chemical reactions. In the examples quoted below, all descriptors for simple elements have been computed through the Gaussian code B3LYP/6-311 + G(d), and a geometrical averaging has been used for more complex compounds (silicate melts).

Fitness landscape diagrams are two dimensional plots on which their coordinates can be used to map a third parameter determining heights or valleys, indicative of instability or stability [14]. They are widely in use in ecological or evolutionary studies. Their introduction in chemistry [15], using electrophilicity and hardness as coordinates, would indicate the trends of maximum hardness of minimum electrophilicity, according to those principles. Nevertheless, this represents a trivial example of what can be read from fitness diagrams. The present paper suggests several other ways of reading such diagrams, simple to use, but offering various insights to chemical reactions.

3. Reading fitness diagrams as binary plots

The simplest way of using such diagrams is through binary plots. For instance, electronegativity (χ) is plotted against hardness (η). Since both coordinates are the first and second derivative of the energy, at a given condition, the diagrams could bear similitude with the resolution of first (or second) order derivative equations. More interesting is the diagram [η - ω] of electrophilicity vs. hardness (Fig. 2). On such a diagram, the two principles of maximum hardness (MHP) and minimum electrophilicity (mEP) indicate the trends reactions should evolve toward.

A second example uses simple ligands formation. Depending on their charge, cations can combine with halogens, or form oxides, sulphur compounds... The chemical descriptors of such compounds have been computed using DFT and plotted onto a [η - ω] diagram (Fig. 3). Their disposition is not fortuitous. Two branches are obviously represented, showing the predominance of ω or η . The two branches link with the domains of electron donors and acceptors (Fig. 3). A simple explanation can be suggested from the dynamic analogy with motion. In case of dominant ω , the acceleration change dominates velocity variation. Thus, according

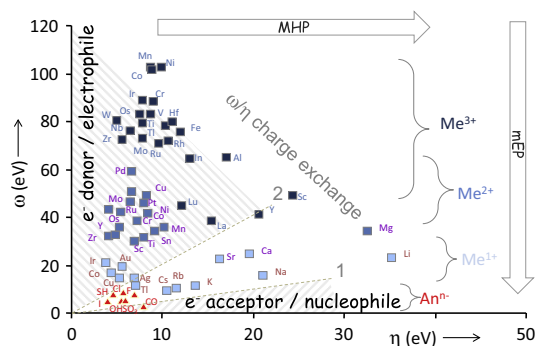


Fig. 2. Binary diagram [η - ω] showing elements according to their charge. Cations are represented by squares, whereas anions are shown by triangles. Metals are figure according to their charge (Me^+ , Me^{2+} and Me^{3+}) with deeper colour. The binary diagram carries more information when indicating the trends of the two principles (maximum hardness, MHP) and (minimum electrophilicity mEP). They are indicated with arrows. It indicates higher electrophilicity (ω) with higher charge. Domains of electron-donor and -acceptor elements are indicated, separated by the maximum charge exchange (ω/η). They provide supplementary information on the evolution of elements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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