

This Week's Citation Classic[®]

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Pearson R G. Hard and soft acids and bases. HSAB, part I: fundamental principles. *J. Chem. Educ.* 45:581-7, 1968.
[Northwestern University, Evanston, IL]

Hard Lewis bases are defined as those where the donor atom is of high electronegativity, and soft bases as those of low electronegativity. Lewis acids may be operationally defined as hard, if they prefer hard bases, or soft, if they prefer soft bases. [The SC][®] indicates that this paper has been cited in over 480 publications. It is the most-cited paper ever published in this journal.]

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This paper was a follow-up to an earlier paper on the same subject that had attracted a great deal of attention.¹ It was intended to be largely pedagogical in nature and my goal was partly to clear up some misconceptions arising from the earlier work. These misconceptions were not unexpected, nor were they unreasonable, since my own views were not clearly delineated at the time of the first paper.

The main idea of both papers was that chemistry could be looked at in a very general way by using the Lewis theory² of acids and bases,



where A is an electron-pair acceptor and B is an electron-pair donor. All chemical bonds could be considered as being formed by the interaction of a suitable A and :B. Any rules that could be developed for predicting the strength of this interaction would be extremely useful.

Bases were defined as hard or soft according to the electronegativity of the donor atom. Hard and soft acids could be defined in a similar way by considering the acceptor

atom. Based on experimental evidence, the following rule was proposed: "Hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases." This rule is known as the Principle of Hard and Soft Acids and Bases (HSAB Principle). It has been widely applied and quoted, usually in a favorable sense.

Sometimes, however, the application does not fit the rule, or does not seem to. Such cases obviously generated some unfavorable comments. One of the things I wanted to do in the second paper was to point out that no one scale of parameters for A and :B, such as hardness or softness, could possibly fit all of the results for this reaction. At the very least two parameters would be needed for each acid or base. As companion parameters for hardness or softness, I suggested intrinsic strength, based mainly on simple electrostatic interactions. Thus H₂O, OH⁻, and O²⁻ would all be hard bases, but oxide ion would be by far the stronger.

While the 1968 paper has been widely quoted, it is not because of what I considered to be this important advance over the 1963 paper. Instead both papers are quoted for the same two reasons: the new terminology of hard and soft acids and bases filled a real need. The HSAB Principle can be applied to so many phenomena that almost any experiment supplies a new case that can be tested.

Finally, it is of interest to point out that R.G. Parr and I have recently supplied a much-needed operational definition of chemical hardness.³ Previously, acids and bases had only been put into broad categories without giving rank orders. The new definition for absolute hardness, η , is

$$\eta = (I-A)/2$$

where I is the ionization potential and the electron affinity of any atom, ion, radical, or molecule. At the same time a companion parameter, the absolute electronegativity, χ , is defined as

$$\chi = (I+A)/2$$

In this way, the necessary two parameters for each acid and base may be found from experimental results of an independent nature.

1. Pearson R G. Hard and soft acids and bases. *J. Amer. Chem. Soc.* 85:3533-9, 1963. [See also: Pearson R G. Citation Classic. *Current Contents/Physical, Chemical & Earth Sciences* 20(23):12, 9 June 1980.]
2. Lewis G N. *Valence and the structure of atoms and molecules*. New York: Chemical Catalog Co., 1923. 172 p.
3. Parr R G & Pearson R G. Absolute hardness: a companion parameter to absolute electronegativity. *J. Amer. Chem. Soc.* 105:7512-16, 1983.