The Challenge to establish a definition

by Pavel Karen

Doing chemistry only makes sense if we communicate the results. That is not so simple; the audience has to understand what we mean. It starts by calling things correct names of precise meaning. What are they? Would a plain dictionary help? Partly. A language dictionary often describes a noun with an array of synonyms of subtly varied meaning as a hint about possible contexts. Language is flexible, and that is fine in everyday life. In natural sciences, however, definitions have to be precise. Like having one for each synonym of that explanatory array in the dictionary. We need a proper definition of our term; a short focused description in well-known simple words that delimit the range of applicability of that term (see also [1]). The definition must primarily be: (a) specific, excluding all cases not covered by the term and including all that are covered, and (b) reflective of the current use of that term as a noun, or also as a verb and adjective if applicable.

That is easier said than done. How to recognize an imperfect definition? Say, someone tries to define the metallurgy term "alloy": **Alloy is a solid containing at least one metal and at least one other element (metal or non-metal); showing the properties of metallic crystals**.

It sounds just fine. Until one considers several solids actually "showing properties of metallic crystals". Are these alloys: (1) golden metallic YC_2; (2) AuCu intermetallic compound; (3) golden metallic oxide TiO; (4) silvery metallic perovskite-type $AuNCa_3$; (5) copper colored ReO_3; (6) metallic carbide Fe_3C; (7) austenite, a solid solution of carbon in fcc γ-iron; (8) brass, a solid solution of zinc in copper?

How do these metallic crystals fulfill the above definition? (a) Is the given crystal an alloy? Alloy of what? (b) Can it be prepared by alloying elements (does "alloy" apply as a verb to the synthesis/manufacturing process)? (c) Is it referred to as an alloy in the literature?

Brass, a solid solution of zinc in copper, is made by alloying; adding Zn to melted Cu. The AuCu, Fe_3C and austenite can too be prepared by alloying elements. They are components of an alloy, crystals of own specific structure, each an alloy of a composition with a relatively narrow homogeneity range. The rest are not really alloys: YC_2 is a metallic salt that hydrolyzes in some similarity to CaC_2. TiO and ReO_3 are never referred to as alloys, and we cannot say that they are prepared by alloying Ti or Re with oxygen. The latter would not even form by such a reaction. Neither is the metallic $AuNCa_3$ salt tricalcium auride(1−)nitride(3−) bis[electride(1−)] referred to as an alloy or a component of an alloy.

And then we must ask: Is "showing the properties of metallic crystals" inclusive of all materials typically referred to as an alloy? Does it include amorphous alloys like Vitreloy or metallic glasses in general? No. So our seemingly OK definition is not very good in clarifying what an alloy is.

Another challenge appears when the term to be defined is a quantity, when it has a numerical value. In communication, the term introduces its quantity value [2], yet the value as such does not necessarily define the term. Besides directly measurable "physical" quantities, we have in chemistry several descriptive terms that acquire various numerical values depending on the chemical composition and structure they refer to. Such a term as a quantity concept has a definition. As a quantity value, it obtains via algorithms; often by one approach of several possible, one that suits the target molecule, ion, or compound. Take bond order as an example. Bond order of two atoms is the (integer or fractional) number of their two-electron bonds equivalent to the given bond. This might be a general definition of the term bond order as a simple heuristic concept for any chemist. However, what is its numerical value? That has to be calculated for each bond by a suitable algorithm; preferably heuristic, easy to grasp and think about, not a black box. In this case, several algorithms exist with simple starting parameters for the two bonded elements: For simple molecules, we draw an MO scheme and subtract electrons in antibonding MOs from electrons in bonding MOs to obtain twice the value of the bond order. That algorithm is also nicely illustrative of the bond order as a concept, and, in a more precise form, it appears in the Gold Book entry [3]. Alternatively, we draw a Lewis formula according to rules (8−N rule applied by order of electronegativities, octet, etc.) while counting electrons to obtain bond orders as integers or simple fractions. Or we calculate a decimal bond order, typically fractional, from the bond length. This too is a heuristic approach when based [4] on those two atoms' Allred–Rochow electronegativities, the difference of which correlates with the covalence-based bond shortening versus the sum of the two "ionic" radii that are fit by least squares to many bond lengths of well-defined bond order between these two atoms. Two parameters for each atom are enough; electronegativity and ionic radius. To relate to the result, we must understand how it was obtained and what it means. We thus need the definition to understand the term bond order as a concept, and we need a heuristic

algorithm to calculate its quantity value. Machines need a program code. The heuristic algorithm for human use cannot be just a black box of quantum-chemical program operating with internal parameters that may vary without obvious link to the actual chemistry investigated. However, if such a program is widely used, a normative work about the term should list it after the heuristic algorithms are given.

For the bond-order and similar chemistry concepts, the algorithm is not a definition. None of the three algorithms mentioned above defines in general what the bond order is; for that their practical use is too narrow. The order of the bond is not always seen from the MO scheme; not necessarily well defined by how we set up a Lewis formula; nor by the bond-valence parameters in Ref. 4 that give precise results for extended solids (structural compromises considering) yet less so for bonds of high order in molecules. The algorithm we actually use merely defines the just calculated quantity value.

So, when a chemistry term is not a directly measurable quantity, its quantity value is linked to an algorithm. The current use may allow several heuristic algorithms to calculate it. Whereas the algorithms can build on various specific approaches and sets of parameters, the concept definition should cover the meaning reflected in the current use of the term, free of possible errors. To describe such a concept in a textbook or compendium, both its definition and the algorithms to calculate its value should be listed; definition first, algorithms afterwards.

What can we do to obtain a good definition in a normative IUPAC work? Quite a lot: (a) Analyze the history of the term, of its meaning, of its use. (b) Analyze the current use of the term (the IUPAC principle of reflectivity) in all grammar forms while looking for possible mistakes or inconsistencies in that use. (c) Analyze composed terms related to the term in question. (d) Analyze a lot of examples—those that fit the term and those that do not—in order to identify the validity limits of the term or the algorithm. (e) Have collaborators who cover the needed competence span and have no conflict of interest about the term being defined. And all that can be fun too!

References

1. How to write standards. Tips for standards writers. ISO, 2016, ISBN 978-92-67-10686-1, https://www.iso.org/files/live/sites/isoorg/files/developing_standards/docs/en/how-to-write-standards.pdf
2. VIM definitions with informative annotations (bipm.org) https://jcgm.bipm.org/vim/en/index.html
3. IUPAC Compendium of Chemical Terminology (https://doi.org/10.1351/goldbook): bond order (https://doi.org/10.1351/goldbook.B00707) https://doi.org/10.1351/goldbook
4. Brese, N.E., O'Keeffe, M., Acta Crystallogr. Sect. B 47(1991) 192–7; https://doi.org/10.1107/S0108768190011041