Nature and Notation: Ewens-Bassett Numbers and Oxidation States of Inorganic Compounds

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Abstract: The Roman numerals used in the Stock nomenclature system and their recent development into oxidation states as members of various Kossel isoelectronic series are compared with the Ewens-Bassett (E-B) numbers. The admittedly restricted area in which E-B numbers are superior to the other notations of inorganic nomenclature is discussed and delineated. In cases where insufficient structural data do not permit an unambiguous decision between molecular and ionic species, the use of the coordination number (N) is advocated.

In the gaseous state at reasonable pressures and temperatures (e. g., below 20 atm and 1000 °C) and in the absence of electric discharges, pure compounds (as well as their mixtures) conform closely to the predicted behavior for ideal gases[1]. Under these circumstances, it is also appropriate to say that the gas consists of molecules, though effects of partial oligomerization are well known for NO_2, HF, and acetic acid vapor. Partly because of the importance of distillation (and, more recently, of gas chromatography and mass spectrometry) for the organic chemist, and partly because of the long conservation time of isomers and enantiomers, it is a prevalent belief that «all compounds consist of molecules». Since the majority of all compounds are organic, it is beyond doubt that most compounds indeed consist of molecules, but it is also true that the majority of carbon-free compounds in condensed phases (liquids or vitreous, amorphous, and crystalline solids) do not contain well-defined neutral molecules, and furthermore, that such systems very frequently are non-stoichiometric. The cubic fluorite-type oxides (ThO_2) and fluorides (CaF_2) can incorporate large amounts of trivalent elements by a statistically disordered anion deficit (e. g., $Th_{1-x}La_xO_{2-0.5x}$) or excess (e. g., $Ca_{1-x}Y_xF_{2+x}$). Another type of non-stoichiometry is charge compensation of constituents with comparable ionic radii; the replacement of $Na^{I} + Si^{IV}$ by $Ca^{II} + Al^{III}$ is commonplace in rocks.

Many coordination compounds clearly consist of polyatomic cations and anions. Such a situation also occurs in salts such as $[N(CH_3)_4]^{\oplus}[B(C_6H_5)_4]^{\ominus}$, but organic nomenclature has chosen to emphasize neutral molecules, disregarding, for example, the fact that the guanidinium ion $C(NH_2)_3^{\oplus}$ is much more usual than guanidine or that cyclopentadienide $C_5H_5^{\ominus}$ is a versatile ligand. Another problem for molecules not bearing any overall charge can be the tautomeric mobility of protons, as found in zwitter-ions of amino acids approaching the intrinsic dipole of betaine $(CH_3)_3NCH_2CO_2$. Generally, inorganic nomenclature has been a pragmatically much less urgent task and has remained far less amenable to systematic rules because of the much smaller number of compounds involved, the frequent lack of detailed knowledge of the structure of many compounds, and the wider variety in properties of a hundred odd elements compared to that of the relatively few elements predominant in organic compounds.

At present, two major strategies applied in attempts to obtain a reasonably coherent inorganic nomenclature of salts of polyatomic cations and anions are: (1) *Stock oxidation states*, written with Roman numerals either as superscripts (such as $Pb_2^{II}Pb^{IV}O_4$ in minium or $S^{-II}S^{VI}O_3^{2\ominus}$ in thiosulfate) or in parentheses (such as Pt(IV) and Cl(−I) in $PtCl_6^{2\ominus}$ or Mn(VII) and O(−II) in $MnO_4^{\ominus}$); and (2) *Ewens-Bassett numbers* giving the charge of a cation or anion in units of the protonic charge *e*. [We are not fully convinced that it is helpful to continue the usage of indicating ionic charges as (3+) and (2−) rather than the algebraic expressions (+3) and (−2) with the sign before the integer, but this note should not be overloaded with these controversial arguments]. In any case, the Ewens-Bassett[2] numbers first proposed in 1949 have been incorporated[3] into the «Definitive Rules 1970 issued by the [IUPAC] Commission on the Nomenclature of Inorganic Chemistry» as a legitimate alternative to the oxidation numbers of individual atoms. Thus, it is clear that species such as $S_4^{2\oplus}$ and $I_5^{\ominus}$ are better described as tetrasulfur(2+) and pentaiodide(1−) ions and that calling $K_2Cu(CCH)_3$ potassium triethynylcuprate(2−) avoids the need for justifying the alternative name, potassium triethynylcuprate(I), according to the Stock system. However, the 1970 rules would permit $K_4(NC)_3NiNi(CN)_3$ to be called potassium tricyanoniccolate(2−) as long as its dimeric nature is uncertain.

In many cases of metal complexes with sulfur-containing ligands[4] such as $M(S_2C_2R_2)_2^{z\ominus}$ and $M(S_2C_2R_2)_3^{z\ominus}$, it is safer to write Ewens-Bassett numbers (2−), (1−), and (0) rather than M(II), M(III), and M(IV) for the rectangular coordination of two bidentate ligands (having the trivial name maleonitrilodithiolate for R = CN) or M(IV), M(V), and M(VI), respectively, for the trigonal prismatic coordination of three ligands of the type colloquially said not be «innocent»[4]. However, it is important to realize that the justification for Ewens-Bassett (E-B) numbers stands or falls with the plausibility of dissecting a compound into cations and anions. Evidence for such a separation can be obtained from physical properties (e. g., electrical conductivity and Raman spectra) of solutions in water (or other highly polar solvents) or from «chemical bonds» much

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shorter than «van der Waals contacts» shown by X-ray or neutron diffraction of a crystal. It is difficult to be certain that solutions and crystals contain the same polyatomic ions, and convincing evidence can sometimes be obtained from characteristic absorption bands of transition-group complexes involving a partly filled d- or f-shell[4–6]. The question of polyatomic cations and anions for (E-B) classification purposes can usually be clarified by consideration of *coordination numbers* (*N*). This integer *N* for a given atom is well-defined in cases of identical distances from the nucleus of the atom to *N* adjacent nuclei, which have the same atomic number *Z*. In cases of differing distances, or the binding of two or more elements, it is to a certain extent a matter of choice how large *N* is, or whether it can be defined at all. Distances greater than 1.1 times the typical bond length are not normally included in evaluating *N*. As a numerical example, the six shortest Cs-Cs distances in CsCl, being 1.1547 times longer than the eight Cs-Cl distances, are not taken into account, but in the analogous case of cubic iron or tungsten, *N* is usually said to be $14 = 8 + 6$, perhaps because it is closer to $4\pi = 12.5664$.

Although organometallic compounds provide interesting cases of $N = 10$, 12, and 16 in sandwiches of two cyclopentadienide, benzene, and cyclooctatetraenide ligands, most monatomic cations[6–11] sufficiently large to show $N = 7, 8, 9, 10, \ldots$ with unidentate ligands (such as water) and aminopolycarboxylate anions generally show pronounced energetic indifference to the local symmetry and the *N* value adopted. It is not possible to determine the actual value of *N* from the formula for a stoichiometric crystal. For example, calcium in $CaCO_3$ has $N = 6$ in the calcite structure and $N = 9$ in aragonite, but $N = 3$ for carbon in both cases. Also, $N = 6$ for hydride in the NaCl-type nonmetallic crystals LiH and CsH and in the perovskites $BaLiH_3$ and $EuLiH_3$. $N = 8$ for carbon in the CaF_2-type amber-yellow nonmetallic Be_2C, but beryllium has $N = 4$ as usual (the reason why *Lewis*' hypothesis (1916) that $2N$ electrons constitute *N* bonds is a rather unreliable extrapolation from aliphatic molecules to most inorganic compounds has been discussed elsewhere[10, 12]).

One of the difficulties in applying Ewens-Bassett numbers is that, unlike $BaCO_3$ or YPO_4, many solid compounds do not contain discrete anions, but instead, the oxygen atoms connect the other elements to a skeleton extending throughout the entire crystal. Although the perovskites $BaTiO_3$, $LaAlO_3$, $KNbO_3$, etc. are frequently called barium titanate, lanthanum aluminate, potassium niobate, etc., they do not contain titanate(2−), aluminate(3−), niobate(1−), etc. as discrete finite anions. The 1970 nomenclature rules present the Stock Roman numerals as a unique alternative to the Ewens-Bassett numbers. A closer analysis[4] shows that the situation is far more complicated. One of at least three major alternatives is the use of *oxidation numbers* (*n*), which serve primarily to equilibrate easily redox equations for inorganic reactions in solution according to a definite scheme proposed by *Rancke-Madsen*[4]. The choice of *n* values involves a few somewhat arbitrary decisions. When $n = +1$ for hydrogen connected only to N, Te, Se, S, I, Br, Cl, O, and F, and $n = -1$ in all other nonmetallic hydrides, the rule is related to the electronegativity (which has verifiable consequences in electron transfer spectra[13] and molecular orbital ionization energies[14, 15] as determined from photoelectron spectra of gaseous and solid compounds). These *n* values can be fractional such as $+\frac{1}{2}$ in $O_2^{\oplus}$ and $Xe_2^{\oplus}$, $-\frac{1}{2}$ in $O_2^{\ominus}$, and $-\frac{1}{3}$ in $N_3^{\ominus}$ and $I_3^{\ominus}$. From the point of view of redox reactions, it is feasible to consider the average $n = 2.66\ldots$ in Pb_3O_4 and Fe_3O_4 and $n = 2$ in $S_2O_3^{2\ominus}$ despite strong evidence for Pb^{II}, Pb^{IV}, Fe^{II}, Fe^{III}, S^{-II}, and S^{VI}. Homonuclear molecules have $n = 0$. The reason that metallic elements also have $n = 0$ is different and related to the rule that the solids are equally well described if the average *n* vanishes. Crystal structure determinations show that pyrite (FeS_2) actually contains Fe^{II} and $SS^{2\ominus}$ and that calomel (Hg_2Cl_2) contains the mercurous dimer and Cl^{-I}, though $n = 1$ can be chosen for mercury.

Many species have a well-defined *n*, but not a well-defined oxidation state (here written with Stock numerals), while other species have the opposite problem. Thus *catenation* between identical atoms is sufficient to prevent defined oxidation states. For example, sulfur has $n = 5$ in F_5SSF_5 and in dithionate, $O_3SSO_3^{2\ominus}$. The pseudohalide behavior shown by the oxidative dimerization of many $RS^{\ominus}$ species to RSSR (as known from cysteine and cystine in biochemistry) is also observed in the titration of I_2 with thiosulfate to form tetrathionate, $O_3SSSSO_3^{2\ominus}$. On the other hand, the characteristic absorption bands of translucid transition-group compounds may indicate the oxidation state corresponding to a definite number of d-like, 4f or 5f electrons. In certain cases, the oxidation state may be evaluated from *N* and the preferred stereochemistry in the d-groups[4]. In metallic elements and alloys, a *conditional oxidation state* may be derived from magnetic properties (and to some extent from molar volumes), indicating the total spin quantum number *S*. In the 4f group (lanthanoids), M[II] can be observed with one 4f electron more than M[III], whereas in the 5f group (transthorium elements), M[III] and M[IV] are the most frequent conditional oxidation states[7, 16, 17].

Some of the motivation behind the Ewens-Bassett numbers is undoubtedly the desire not to go beyond the data; for example, pentacyanohydridocobaltate(3−) being more non-committal than pentacyanohydridocobaltate(III). It is fashionable to employ a mental restriction like «formal oxidation number» for the oxidation state, as if the windmill to fight were a completely ionic picture. Actually, the oxidation state of atoms in gaseous and solid compounds is comparable[4, 18] to the «preponderant electron configuration» correctly describing quantum numbers of the manifold consisting of the ground state and the lower-lying excited states of a monatomic entity, despite the correlation effects preventing the wave-function from being a Slater determinant corresponding to a definite electron configuration, such as $1s^22s^2$ for the ground state of the beryllium atom.

In successful cases, the oxidation state is directly related to observed properties. Recently, a list[19] of 315 oxidation states arranged in 81 isoelectronic series with *Kossel electron numbers* (*K*) from zero (H^I), 2 (H^{-I} to N^V), up to $K = 100$ (No^{II}, Lr^{III}, ...) was compiled for compounds at moderate temperature (excluding species in cool matrices and in very hot vapors, also ions only observed in mass spectra) *which are not catenated and do not show metallic conductivity*. When applicable, such oxidation states and *K* values contain more information than «external» charges expressed as Ewens-Bassett numbers. On the other hand, E-B numbers remain useful for naming compounds in the fringe area where evidence for oxidation states has not yet been obtained (or is known to be inaccessible) and in particular for cations and anions containing only nuclei with the same *Z*, or a combination of nuclei (e.g., $BrI_2^{\ominus}$) of chemically closely similar elements.

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