Technical Note: Does Cr^{6+} Really Exist? Difference Between Charge and Oxidation State and How to Record Them

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Terms such as "charge" and "oxidation state" appear frequently in the literature. The problem is that they are often viewed to be synonymous. However, they are fundamentally different concepts using distinct notations. The aim of the present discussion is to attract the attention of researchers from various fields of science in order to prevent further use of misleading interpretations.

KEY WORDS: chromate, oxidation, oxidation charge, oxidation state

DISCUSSION

More and more incorrect use of chemical nomenclature has appeared in the last decades in the scientific literature concerning the field of corrosion. Specifically, incorrect notations and even scientific misinterpretations associated with the chemical terms "charge" and "oxidation state" are noted. This can be seen not only in high-ranking scientific journals concerned with the field, but also in the records of international conferences presented to eminent audiences. Once published, these incorrect entries persist, being cited and spread further without being recognized as incorrect. One of the main contributing factors to these mistakes or even misunderstandings may be related to the fact that the corrosion researchers have different backgrounds, not necessarily the most frequent being in chemistry, but in other fields important in corrosion research, such as material science, metallurgy, engineering, and physics. This is obviously related, not only to the authors of the scientific papers, but also to the reviewers and editors, who are responsible for the correct use of scientific terms. Another problem may be simply an insufficient level of accuracy, which is not acceptable in scientific records. The auto-detrimental effect caused by the accumulation of incorrect records is evident in the literature. It is thus of great interest to produce scientifically accurate papers that obey the IUPAC(1) notation. The present discussion is aimed to attract the attention of researchers from various fields of science to prevent further use of misleading notations and interpretation. Further, its purpose is to bridge the gap between the academic and industrial backgrounds in presenting the established results of research to a wide audience. It relates to all areas of science in which the chemistry of aqueous solutions comes to the fore, although the motivation for writing this note comes from the field of corrosion and corrosion protection of metals.

One of the main questions is, which form of the ions would be correct to use in the chemical notations? A few dilemmas are (Cu^{2+} or Cu^{+2}), (Cr^{6+} or Cr^{+6}, Cr^{VI} or CrO$_4^{2-}$) and (MoO$_4^{2-}$ or MoO$_4^{-2}$). The choice depends on what needs to be expressed.

First to consider and differentiate are the two terms, the charge and the oxidation state (Table 1). If an atom gains or loses electrons, it may become a cation, an ion with a positive charge, or an anion, i.e., an ion with a negative charge. Note that the authors are here referring mainly to oxidation-reduction reactions in aqueous solution.(2) According to the IUPAC, the position of the charge is in the right upper index (superscript) following the chemical symbol. The magnitude of the charge of an ion is given in Arabic numerals, followed by the sign of the charge, e.g., Cu^{2+}, MnO$_4^{2-}$. The signs plus (+) and minus (−)(3) are used to indicate the charge of an ion written as a symbol, or in its written form, e.g., Al^{3+}, Al(3+) or aluminum (3+). The definition and correct record of the charge are given in Table 1 for several types of ions.[1-2]

On the other hand, the concept of oxidation state (oxidation number) is a formalism.(4) The oxidation state is defined

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(1) International Union of Pure and Applied Chemistry, https://iupac.org/.

(2) The anions and cations are not necessarily the consequence of a change in oxidation state. Cr$^{3+}_{(aq)}$ species can be obtained by dissolution of solid Cr(OH)$_3$ in strong acidic conditions.

(3) A minus sign should be written with symbol (−) and not a hyphen sign with symbol (-) or an en-dash sign with symbol (–).

(4) The oxidation state gives the degree of oxidation of an atom in terms of counting electrons. It is defined using the ionic approximation of bonds. An alternative term is the oxidation number. These terms are largely synonymous and are usually used interchangeably, which is also the case in the present text. It may be preferred to use the term oxidation number when it refers to the specific numerical value or parameter assigned to the entity of oxidation state.[5] This is analogous to the use of the term charge number as the numerical value assigned to the entity of ionic charge.[6]

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Table 1. *Definition and Examples of Correct Records for Charge and Oxidation State for Various Types of Ions*

	Charge	**Oxidation State**
Definition	The net electrical charge of an atom.	The charge of an atom in a molecule after ionic approximation of its heteronuclear bonds.
Examples		
Type of Ion	**Charge**	**Oxidation State**(A)
Monoatomic cations		
copper(2+)	Cu^{2+}	Cu(II)
chromium(3+)	Cr^{3+}	Cr(III)
vanadium(3+)	V^{3+}	V(III)
Heteropolyatomic cations		
ammonium	NH_4^+	N(−III), H(I)
hydronium	H_3O^+	H(I), O(−II)
vanadyl	VO^{2+}	V(IV), O(−II)
pervanadyl	VO_2^+	V(V), O(−II)
Monoatomic anions		
chloride(1−) or chloride	Cl^-	Cl(−I)
oxide(2−) or oxide	O^{2-}	O(−II)
Heteropolyatomic anions		
chromate	CrO_4^{2-}	Cr(VI), O(−II)
molybdate	MoO_4^{2-}	Mo(VI), O(−II)
orthovanadate	VO_4^{3-}	V(V), O(−II)

(A) Acceptable records are given for the examples of chromium in chromate: Cr^{VI}, Cr(+6), and Cr^{+6}, and oxygen in chromate: O^{-II}, O(−2), and O^{-2}.

as the charge of an atom in a molecule after ionic approximation of its heteronuclear bonds.[1,3] In other words, it is the hypothetical charge an atom would have if all bonds to atoms of different elements were treated as ionic.[4] The oxidation numbers are denoted by the Roman numerals in parantheses after the element name, e.g., Cr(VI). Note that there is no space between chemical symbol and parenthesis. An oxidation number so written is always non-negative unless the minus sign is explicitly used (the positive sign is never used). An oxidation number of zero may be represented by the numeral 0, but this is not usually shown. Alternatively, Roman numerals can be written as a right-hand superscript,[7] e.g., Cr^{VI}, or as Arabic numerals preceded by the appropriate charge sign,[2-3] e.g., Cr(+6) and Cr^{+6}, or by placing the oxidation number exactly above the appropriate chemical symbols (see Table 2). Therefore, records given in Table 2 such as Cr^{VI}, Cr(+6), and Cr^{+6} are not incorrect but are not strictly according to IUPAC. De facto, they are the tool for easier notation of the oxidation number of a chemical element in a formula or a compound.[2] As such, these records do not break the IUPAC rules and therefore could be considered as the acceptable extension to the rule.

To summarize, a Roman numeral or an Arabic numeral preceded by a plus or a minus sign denotes the oxidation number and should not be confused by a numeral followed by a plus or a minus sign, which denotes the charge.

Look now, as an example, at sodium chromate, Na_2CrO_4. The total charge of this compound is neutral because the sum of all of the oxidation numbers for $[(Na^{+1})_2Cr^{+6}(O^{-2})_4]$ comes to zero. Refer to the footnote for a proper record of chemical reactions.(5) In aqueous solution, two charged species exist, Na^+ (cation) and CrO_4^{2-} (anion), i.e., sodium(1+) and chromate(2−). It is of paramount importance to note that, in chromate, the chromium atom does not have the charge of a bare cationic species (Cr^{n+}), but has that of an oxyanion (CrO_4^{2-}) one. Thus, the charge of a chromate anion is 2− and the oxidation number of chromium is +6, i.e., Cr(VI) or Cr^{+6}. This is presented illustratively in Table 2.

In the literature, the form Cr^{6+} is often used in relation to chromate species, chromate conversion coating, etc. The use of a notation such as Cr^{6+} is misleading and incorrect because it represents the ionic species (Tables 1 and 2). In fact, the authors intended to represent the chromium species as chromate ions (CrO_4^{2-}) or chromate compounds, Cr(VI). The records such as "chromate Cr^{6+}," "Cr^{6+} species," or "chromium 6+" actually imply that chromate CrO_4^{2-} contains a Cr^{6+} ion, which is incorrect. Common mistakes are also: "the standard potential of $Fe^{+3/+2}$," "Cr in the 3+ oxidation state," insoluble Cr^{3+} compound," etc. The problem lies in the fact that the charge of an ion and its oxidation state are used interchangeably.[9] This work will explain this issue in more detail to further avoid such misconceptions or misinterpretations.

Chromium exhibits a wide range of possible oxidation states, of which the +3 and +6 states are the most commonly observed in its compounds. Furthermore, chromium ions exist in aqueous solution in the form of positively charged particles (cations) and negatively charged particles (anions). In the second part of the present paper, the possible existence of chromium ions with charges of 3+ and 6+ is discussed. The mono atomic ion, Cr^{3+}, exists in aqueous solution, but the Cr^{6+} does not. A very high positive charge, included in a hypothetical scenario, would require a prohibitively large amount of energy, which equals the sum of the first six ionization energies of Cr, (652.9 + 1,590.6 + 2,987.0 + 4,743.0 + 6,702.0 + 8,744.9) kJ/mol = 25,420 kJ/mol.[10] The chromium atom in such a high oxidation state is unstable, and it can only be stabilized in an aqueous solution by the most electronegative atoms, such as oxygen. That is why, in aqueous solutions, chromium(VI) (or Cr^{+6}) exists as polyatomic ions, i.e., oxyanions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). The oxo ligands form formal double bonds with the metal, and the short M−O distances that result allow efficient transfer of charge to the electron-deficient metal center.[4] This is clearly seen in Figure 1 that shows the valence electron charge density of hydrated CrO_4^{2-}(aq) calculated using density functional theory (DFT). Notice a high valence electron density around the Cr nucleus, although Cr is formally in a +6 oxidation state.

The simple experimental evidence would be observation of the vivid colors resulting from the chemistry of transition metal complexes. Their partially filled d orbitals are involved in generating the color arising from d-d transitions, i.e., transfer of electrons from one metal orbital to another (Figure 2).

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(5) Another common mistake in scientific literature is the writing of chemical reactions in italic style. For example:[8] *$HCrO_4^- \rightarrow HCrO_4^{2-} + H^+$* should be written as $HCrO_4^-$ $HCrO_4^{2-} + H^+$. Just because our word processors offer *italic* as the default style in Equation tools does not mean that it is aligned with rules in chemical nomenclature.

Table 2. *Examples of Correct and Incorrect Records for Charge and Oxidation States for Cr(III) and Cr(VI)*

Ion	Charge of Ion in Aqueous Solution (Correct Record)	Charge of Ion in Aqueous Solution (Incorrect Record)	Oxidation State of Chromium (Correct Record)	Oxidation State of Chromium (Incorrect Record)
Cr^{3+} chromium(3+) or chromic ion	3+	+3	Cr(III) acceptable: Cr^{III} Cr(+3) $\overset{+3}{Cr}$ Cr^{+3}	Cr^{3+} Cr(3+)
CrO_4^{2-} chromate	2−	−2	Cr(VI) acceptable: Cr^{VI} Cr(6+) $\overset{+6}{Cr}$ Cr^{+6}	Cr^{6+} Cr(6+)

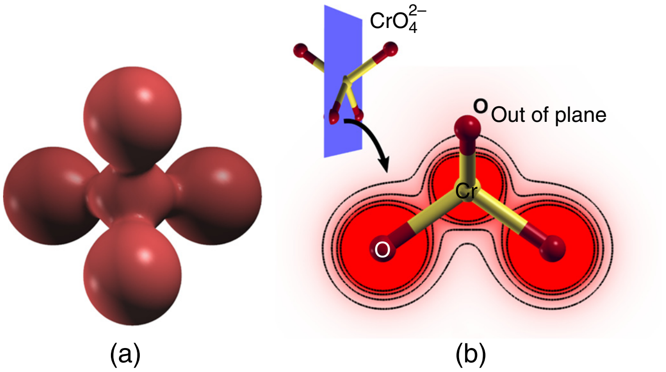

FIGURE 1. *DFT-calculated valence electron charge density of hydrated CrO_4^{2-}. A 3D isosurface of 0.1 e/Bohr^3 is shown in (a), whereas (b) shows 2D contours in linear scale from 0 to 0.2 e/Bohr^3 with the increment of 0.05 e/Bohr^3. Notice a high valence electron density around the Cr nucleus, although Cr is formally in a +6 oxidation state. Bader analysis reveals that Cr and O have 3.2 and 7.2 valence electrons, respectively, hence their charges are 2.8+ and 1.2−.* (Courtesy of Anton Kokalj from Jožef Stefan Institute.)

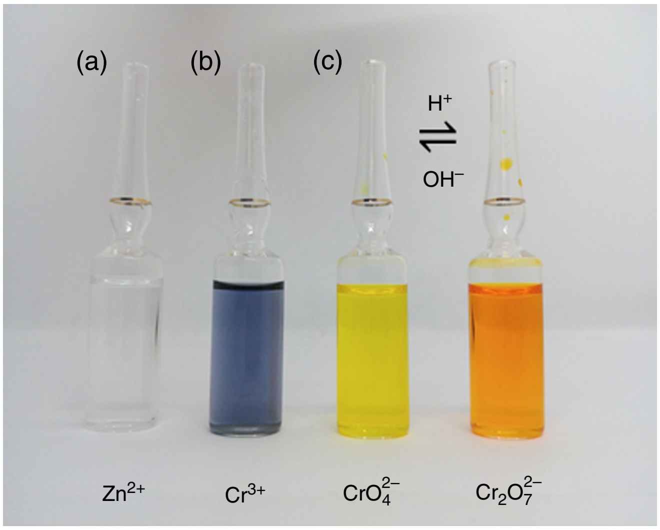

FIGURE 2. *The color of various aqueous solutions: colorless Zn^{2+} (d^0 system, no d-d transitions) (a), violet-blue-gray Cr^{3+}, i.e., $Cr(H_2O)_6^{3+}$ (d^3 system, d-d transitions) (b), and yellow CrO_4^{2-} and orange $Cr_2O_7^{2-}$ (d^0 system, ligand-metal charge transfer) (c).*

For instance, an aqueous solution of Cr^{3+} ions, representing the d^3 system, exhibits a striking violet-blue-gray color. In contrast, if Cr^{6+}, or more correctly $[Cr(H_2O)_6]^{6+}$, existed, it would be colorless in an aqueous solution because of its d^0 configuration, as in the case of nontransition metal ions (Na^+, Mg^{2+}) and transition metal ions, which do not have partially filled d orbitals (Sc^{3+}, Cu^+, Zn^{2+}) (Figure 2). It is, however, well known that the Cr(VI) species are yellow and orange, depending on the pH of the aqueous solution, i.e., on the equilibrium between chromate(VI), CrO_4^{2-}, and dichromate(VI), $Cr_2O_7^{2-}$ (Figure 2). The colors of these species therefore cannot arise from d-d transitions. They are actually associated with electron transfer from the ligand (in this case, O^{2-}) to the central metal atom, Cr(VI), i.e., ligand-metal charge transfer.[11]

Note that a metal ion in aqueous solution is a cation of chemical formula $[M(H_2O)_n]^{z+}$, due to the presence of solvent molecules strongly coordinated to a metal center. However, for the sake of simplicity, these species are refered to as M^{z+} ions.

Finally, the oxidation state does not always have the same magnitude as the charge on the ion. A simple illustration is provided by the vanadium element, which possesses multiple oxidation states. The vanadium in V^{2+} and V^{3+} ions have oxidation states of +2 and +3, respectively. Vanadium, however, in vanadyl VO^{2+} and pervanadyl VO_2^+ ion forms, has an oxidation state of +4 and +5, respectively. The analogy is also valid for CrO_4^{2-} and $Cr_2O_7^{2-}$ oxyanions, as mentioned earlier.

This discussion covers, specifically, an example of chromate, although many other examples can be found. It should be noted that the IUPAC nomenclature used here is applied strictly to this particular example and, for further insights, the IUPAC nomenclature should be consulted and followed closely.[1]

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References

1. A.D. McNaught, A. Wilkinson, “IUPAC. Compendium of Chemical Terminology,” *The Gold Book*, 2nd ed. (Oxford, United Kingdom: Blackwell Scientific Publications, 1997).
2. L. Pauling, *General Chemistry*, 3rd ed. (New York, NY: Dover Publications, Inc., 1969).
3. P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, *Shriver and Atkins’ Inorganic Chemistry*, 5th ed. (New York, NY: Oxford University Press, 2010).
4. G. Parkin, *J. Chem. Educ.* 83 (2006): p. 791-799.
5. P. Karen, P. McArdle, J. Takats, *Pure Appl. Chem.* 88 (2016): p. 831-839.
6. W.B. Jensen, *J. Chem. Educ.* 88 (2011): p. 1599-1600.
7. M. Gerloch, E.C. Constable, *Transition Metal Chemistry: The Valence Shell in d-Block Chemistry* (Weinheim, Germany: Wiley-VCH, 1994).
8. P. Zuman, *Standard Potentials in Aqueous Solution*, eds. A.J. Bard, R. Parsons, J. Jordan (New York, NY: Marcel Dekker, Inc., 1985).
9. A. Kokalj, *Acta Chim. Slov.* 61 (2014): p. 340-349.
10. D.R. Lide, *CRC Handbook of Chemistry and Physics*, Vol. 85 (Boca Raton, FL: CRC Press, 2004).
11. G. Miessler, D.A. Tarr, *Inorganic Chemistry*, 3rd ed. (Upper Saddle River, NJ: Pearson Prentice Hall, 2004).