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# ANALYSIS OF THE STEPS OF THERMAL DECOMPOSITION OF OXO-COMPOUNDS OF THE dsp BLOCK ELEMENTS

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## Abstract

Analysis of thermal decomposition of manganates(VII) and chromates(VI) in terms of the Górski's morphological classification was used to distinguish typical steps of decomposition of oxides and oxo-salts of dsp block elements and to determine the effect of cationic counterions on decomposition of chromates(VI).

**Keywords**: dsp block elements, oxo-compounds

## Introduction

Macroscopic mechanisms of thermal decomposition of solid compounds, such as salts or oxides, are very complex. The decomposition consists of a number of physical and chemical processes involving mass transfer (diffusion) and heat transfer (destruction and formation of crystal lattices, formation of gas phases, rupture and formation of covalent bonds in species of starting materials and reaction products, or exchange of heat with the environment). Thus, the macroscopic mechanisms of decomposition are influenced by the physical conditions of performing the process (isothermal or non-isothermal processes, kind of atmosphere and its pressure), sample mass and shape, surface development, etc. The most substantial, primary part of the macroscopic mechanism of decomposition of chemical compounds is its purely chemical part, consisting in transformation of the structural units of the compound, thus the mechanism of decomposition at the molecular level. If, in the course of heating, the species of the compound are not transformed, only polymorphic changes – melting or evaporation take place. A study of the mechanism of decomposition of solid compounds at the level of molecules is, at present, almost impossible. The species of compounds formed during thermal decomposition, before being transformed into stable species of final compounds, suitable for chemical identification, pass through a series of intermediate species, which usually can

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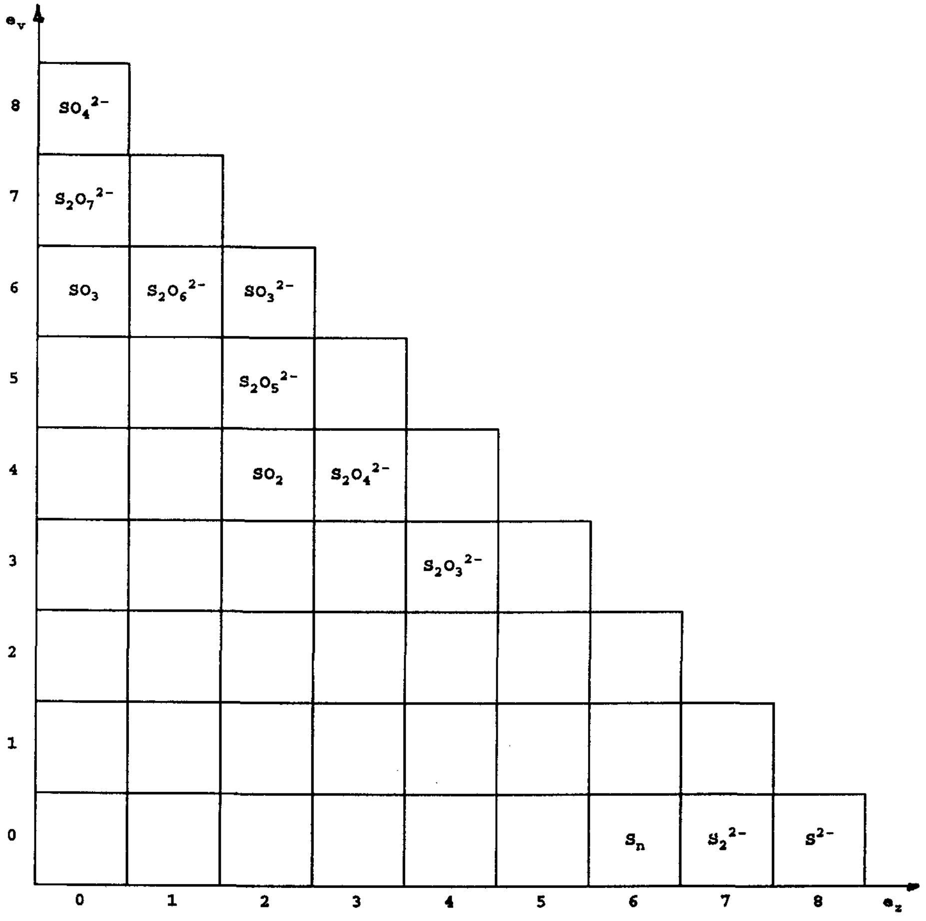
not be identified because of low concentration in the reaction zone. Even in cases, where some intermediate species can be identified, e. g. by the EPR method, there is always a doubt if just these species should be taken into consideration in the basic mechanism of the reaction. The so-called intermediate products, identified in many cases during thermal decomposition of compounds as definite phases and referred to in descriptions of reaction mechanisms, are usually products of reaction performed under altered conditions (at lower heating rate, under reduced pressure, etc.).

In the system involving the definition of chemical element based on the notion of atomic core, the morphologic classification proposed by Górski, and the resulting consistent definition of acid-base and redox reactions [1–4], chemical reactions considered at a molecular level consist in changes of the valency electron environment of the atomic cores.

A transformation of a given simple oxo-species of an element into another simple species may be expressed in terms of some elementary processes connected with transfer of electrons (the redox reactions), $O^{2-}$ ligand (the acid-base reactions), or oxygen atoms (the redac-oxbas reactions). Such transformations are most readily analyzed on the background of classification diagrams which comprise all oxo and oxygen-less simple species of the given element, stable in chemical compounds. Such diagrams are constructed on the basis of two classification coordinates (axes) $e_v$ and $e_z$, which determine the number of elementary charges bound in the valency states of the given element in the form of free electrons ($e_v$) or oxide ligands ($e_z$). In this way the classification diagram represents the whole system of oxo-compounds and oxygen-less species and any transformation of species of a given element may be represented in the diagram as a change of corresponding co-ordinates. In the system defined in this manner there exist structural relationships between individual primary species which are, in addition, related mutually by elementary chemical transformations. These transformations can sometimes lead through unstable species in chemical compounds, but these species should also be taken into account in considering the mechanism of reactions at the molecular level. Such a type of analysis has made it possible to give a consistent representation of decomposition of anionic sub-lattice of most oxo-salts of more electronegative elements of the sp block (Cl, Br, I, S, Se, N, P, As, C). It has enabled also to determine the effect of cationic counterions on the course of the decompositions [5–12].

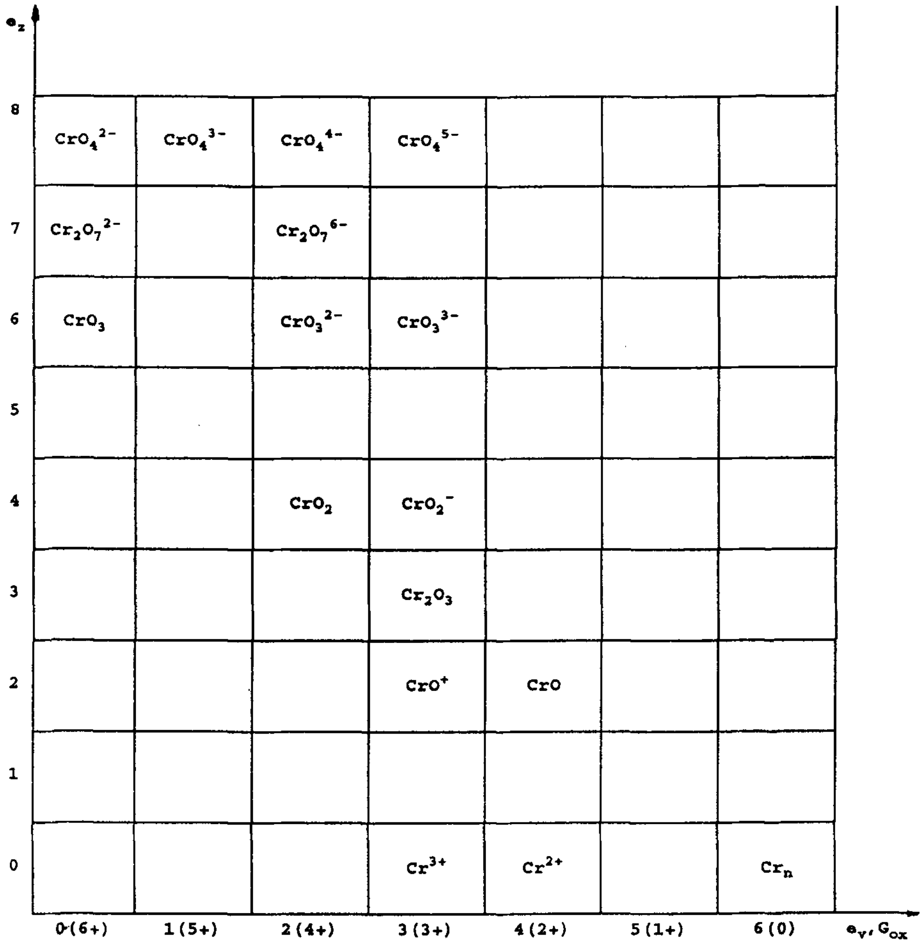
The presented paper is an attempt of applying such an approach to analysis of thermal decomposition of oxides and oxo-salts of the dsp block elements, taking as example the oxo-compounds of chromium and manganese. The different structure of valency states of these two elements, as compared with the structure of the sp block elements, results in the difference of the decomposition mechanisms. These differences arise from different way of filling the valency shells of atomic cores of the sp and dsp block. Free electrons and bonding electron pairs fill arbitrarily the valency states of atomic cores of the sp block elements, whereas in the dsp block the free electrons occupy merely the d orbitals and bonding electron pairs engage free dsp orbitals. This is the source of apparent differences of classification diagrams representing oxo-compounds of sp elements, such as e. g. sulfur (Fig. 1) and those of chromium (Fig. 2) or manganese (Fig. 3) belonging to the dsp block.



| $e_v$ |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| 8 | $SO_4^{2-}$ |  |  |  |  |  |  |  |  |
| 7 | $S_2O_7^{2-}$ |  |  |  |  |  |  |  |  |
| 6 | $SO_3$ | $S_2O_6^{2-}$ | $SO_3^{2-}$ |  |  |  |  |  |  |
| 5 |  |  | $S_2O_5^{2-}$ |  |  |  |  |  |  |
| 4 |  |  | $SO_2$ | $S_2O_4^{2-}$ |  |  |  |  |  |
| 3 |  |  |  |  | $S_2O_3^{2-}$ |  |  |  |  |
| 2 |  |  |  |  |  |  |  |  |  |
| 1 |  |  |  |  |  |  |  |  |  |
| 0 |  |  |  |  |  |  | $S_n$ | $S_2^{2-}$ | $S^{2-}$ |
|  | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 $e_z$ |

**Fig. 1** Classification diagram of oxo species of sulphur

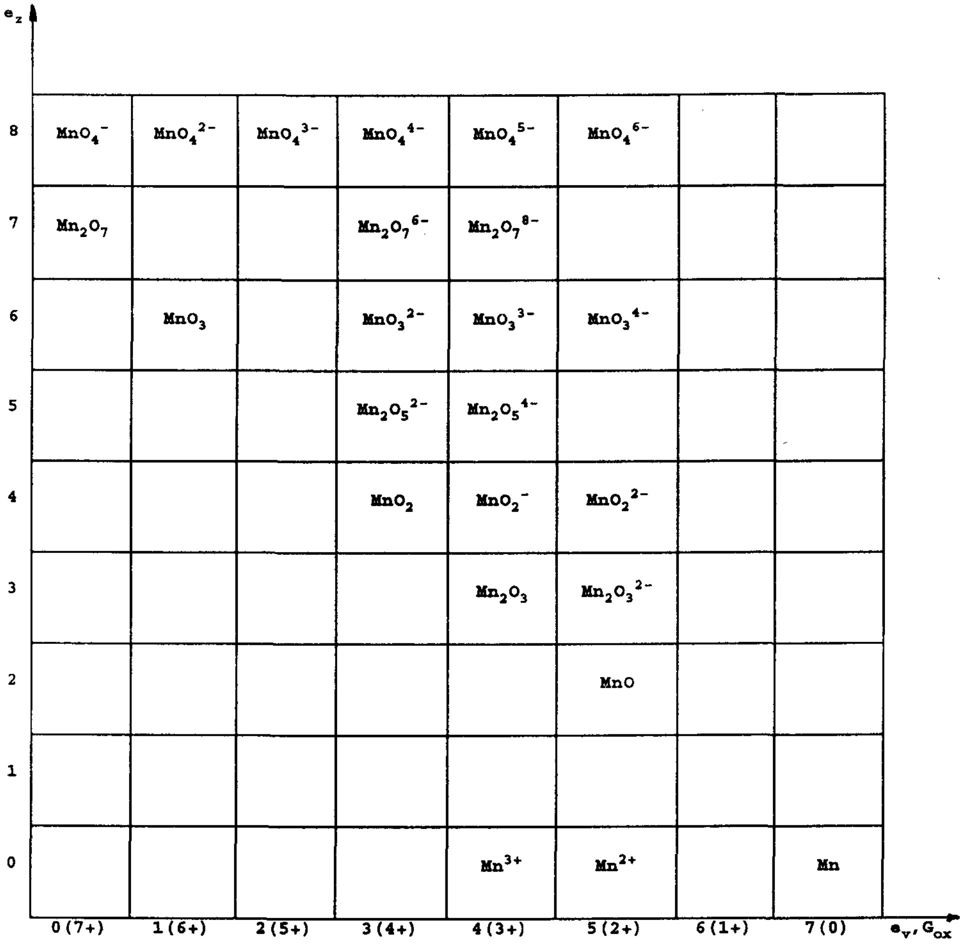
The above figures comprise all the oxygen-containing simple species of sulphur, chromium and manganese, occurring in familiar salts (irrespective of the kind of cations counterions involved) and in oxides. Evidently, if we consider salts with a definite sort of cationic counterion the number of stable anionic



| $e_z$ | 0(6+) | 1(5+) | 2(4+) | 3(3+) | 4(2+) | 5(1+) | 6(0) |
|---|---|---|---|---|---|---|---|
| 8 | $CrO_4^{2-}$ | $CrO_4^{3-}$ | $CrO_4^{4-}$ | $CrO_4^{5-}$ | | | |
| 7 | $Cr_2O_7^{2-}$ | | $Cr_2O_7^{6-}$ | | | | |
| 6 | $CrO_3$ | | $CrO_3^{2-}$ | $CrO_3^{3-}$ | | | |
| 5 | | | | | | | |
| 4 | | | $CrO_2$ | $CrO_2^-$ | | | |
| 3 | | | | $Cr_2O_3$ | | | |
| 2 | | | | $CrO^+$ | $CrO$ | | |
| 1 | | | | | | | |
| 0 | | | | $Cr^{3+}$ | $Cr^{2+}$ | | $Cr_n$ |

**Fig. 2** Classification diagram of oxo species of chromium

sublattices may be limited by the chemical properties of both the cationic and the anionic sublattices. It would be difficult to obtain e. g. $Ag_2S_2O_4$ because of too strongly reductive properties of $S_2O_4^{2-}$ ions with respect to strongly oxidizing cation $Ag^+$. The same holds also for obtaining $Ag_4CrO_4$. In many cases also strongly acidic properties of cations make it impossible to stabilize anionic sublattices of basic nature, e. g. in $Al_2(SO_3)_3$ or $Mg_2MnO_3$. The limitation may also arise from impossibility of stabilization of the anionic sublattice of a salt with a definite cation for the reason of geometry. This is especially true for polymeric threedimensional anionic sublattices. For example, chromium can easily form compounds with polymeric anionic sublattice $CrO_3^{3-}$ with a number of trivalent cations ($La^{3+}$, $Nd^{3+}$..), but similar salts with monovalent or divalent cations are unknown.



| $e_z$ | 0(7+) | 1(6+) | 2(5+) | 3(4+) | 4(3+) | 5(2+) | 6(1+) | 7(0) |
|---|---|---|---|---|---|---|---|---|
| 8 | $MnO_4^-$ | $MnO_4^{2-}$ | $MnO_4^{3-}$ | $MnO_4^{4-}$ | $MnO_4^{5-}$ | $MnO_4^{6-}$ | | |
| 7 | $Mn_2O_7$ | | | $Mn_2O_7^{6-}$ | $Mn_2O_7^{8-}$ | | | |
| 6 | | $MnO_3$ | | $MnO_3^{2-}$ | $MnO_3^{3-}$ | $MnO_3^{4-}$ | | |
| 5 | | | | $Mn_2O_5^{2-}$ | $Mn_2O_5^{4-}$ | | | |
| 4 | | | | $MnO_2$ | $MnO_2^-$ | $MnO_2^{2-}$ | | |
| 3 | | | | | $Mn_2O_3$ | $Mn_2O_3^{2-}$ | | |
| 2 | | | | | | MnO | | |
| 1 | | | | | | | | |
| 0 | | | | | $Mn^{3+}$ | $Mn^{2+}$ | | Mn |

**Fig. 3** Classification diagram of oxo species of manganese

The chemical properties of simple species collected in the classification diagrams (for definite cationic counterions) change in a regular manner if appropriate series are compared. For example, in a series of chromium oxo-compounds at maximum oxidation state both the oxidative and acidic properties increase with decreasing $e_z$ from $CrO_4^{2-}$ through $Cr_2O_7^{2-}$ to $CrO_3$. The basicity of the compounds changes in the reverse order, and such would also be the change of reductive properties if it were a series of simple species at a lower oxidation state. It is a general regularity that the strongest oxidants and the strongest acids at a definite oxidation state are always the oxides, and the strongest bases and reductors are the species having the maximum values of $e_z$. Also, if we compare the simple species having the same value of $e_z$, e. g. a series of manganese species: $MnO_4^-$, $MnO_4^{2-}$, $MnO_4^{3-}$, $MnO_4^{4-}$, $MnO_4^{5-}$, $MnO_4^{6-}$, their basic properties increase with decreasing degree of oxidation. Their reductive properties increase to a degree depending on the symmetry of filling of the d orbitals. Such a type of correlation can also be seen if we compare the properties and the structures of oxo-species of different elements at definite values of $e_z$ and either oxidation degrees or $e_v$ values.

The large number of information available in chemical literature and in data bases, concerning the structures of chemical compounds, their thermal behaviour, reactivity in solution and in the solid phase, makes it possible now to set up a complex analysis of chemical reactivity, at the level of simple species, of all the oxo-compounds of a given element, in the case of anions for given cationic counterions, and also to determine the effect of counterions on the changes in their reactivity.

Let us try to trace the steps of thermal decomposition of chromate(VI) and manganate(VII) anions [13] with the use of the classification diagrams (Figs 2 and 3). Anhydrous manganates(VII) of cations of the 1st and the 2nd group of the periodic table (Li–Cs), Ba–Ca) undergo thermal decomposition in temperature range 200–350°C with evolution of oxygen and formation of manganate(VI):

$$2MnO_4^- \rightarrow MnO_4^{2-} + MnO_2 + O_2$$

Among anhydrous chromates(VI), which can be obtained with a large number of cations, it is possible to distinguish several groups yielding identical products in the course of thermal decomposition.

The 1st group comprises the following chromates(VI): $Na_2CrO_4$, $K_2CrO_4$, $Rb_2CrO_4$, $Cs_2CrO_4$, and $Ag_2CrO_4$ which melt on heating. Their decomposition proceeds in liquid phase and is accompanied by partial evaporation. An exception is $Ag_2CrO_4$, which decomposes according to the following balance equation:

$$Ag_2CrO_4 \rightarrow AgCrO_2 + Ag + O_2$$

The 2nd group comprises $Li_2CrO_4$, $BaCrO_4$, $SrCrO_4$ and $CaCrO_4$, which decompose, with liberation of oxygen, to form chromates(V) and chromates(III), e. g.:

$$4SrCrO_4 \rightarrow Sr_3(CrO_4)_2 + SrCr_2O_4 + 2O_2$$

To the 3rd group belong the chromates(VI) of yttrium, lanthanum and the lanthanons, which decompose with liberation of oxygen and formation of chromates(V) and $Cr_2O_3$:

$$2La_2(CrO_4)_3 \rightarrow 4LaCrO_4 + Cr_2O_3 + 2.5O_2$$

Group 4th are the chromates(VI) formed with strongly acidic cations $M^{2+}$ ($Mg^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Cu^{2+}$ ...), which decompose with liberation of oxygen and formation of chromates(III), with spinel structure, and oxides MO:

$$2MgCrO_4 \rightarrow MgCr_2O_4 + MgO + 1.5O_2$$

Group 5th, which comprises chromates(VI) of cations with the strongest acidic properties, e.g. $Sc_2(CrO_4)_3$, decomposes with formation of corresponding oxides:

$$2Sc_2(CrO_4)_3 \rightarrow 2Sc_2O_3 + 3Cr_2O_3 + 4.5O_2$$

The above presented review shows that the decomposition of chromates(VI) is strongly influenced by cationic counterions. The cations are also responsible for the change of temperature ranges of the decompositions: the stronger are the acidic properties of the cations the lower is the decomposition temperature, from 1300°C for $BaCrO_4$ to about 500°C for $Sc_2(CrO_4)_3$.

An analysis of classification diagrams and positions of both initial anions $MnO_4^-$ and $CrO_4^{2-}$ on one side and corresponding species in the decomposition products – $MnO_4^{2-}$ and $MnO_2$, and $CrO_4^{3-}$, $CrO_2^-$ and $Cr_2O_3$, respectively, makes it evident that transformations of the starting anions must proceed through many intermediate steps, and the decomposition is of disproportional nature. Let us analyse the elementary steps, through which these decompositions may proceed.

The first step in decomposition of anionic sublattices of $MnO_4^-$ and $CrO_4^{2-}$ is the liberation of oxygen:

$$MnO_4^- \rightarrow MnO_3^- + O \qquad (1)\ \text{Fig. 4}$$

$$CrO_4^{2-} \rightarrow CrO_3^{2-} + O \qquad (1)\ \text{Fig. 5}$$

In both cases the primary species formed are unstable in macroscopic systems under normal pressure. Compounds with anionic sublattice $MnO_3^-$ have not been obtained, as yet, and compounds containing polymeric anions $CrO_3^{2-}$ can be obtained only under high pressure, as e. g. $BaCrO_3$. In either case further evolution of oxygen is impossible because of the change of oxidation number of manganese and chromium by two units, owing to attachment of two electrons in

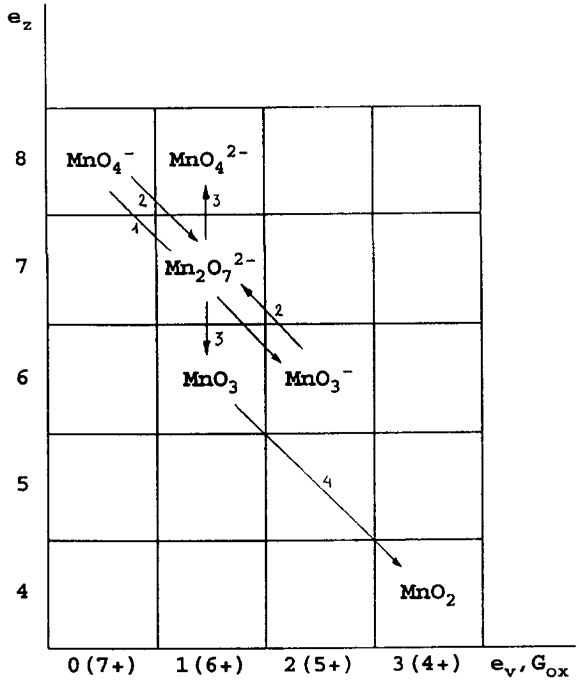


**Fig. 4** Steps in decomposition of anionic sublattice of $MnO_4^-$

valency orbitals d in atomic cores of manganese and chromium. The species $MnO_3^-$ and $CrO_3^{2-}$ with incomplete coordination shells will undergo further transformations, among which the most probable are those involving reactions with undecomposed initial anions:

$$MnO_3^- + MnO_4^- \rightarrow Mn_2O_7^{2-} \qquad \text{(2) Fig. 4}$$

$$CrO_3^{2-} + CrO_4^{2-} \rightarrow Cr_2O_7^{4-} \qquad \text{(2) Fig. 5}$$

to form transitional, two-core species, which also are unstable and unknown in stable salt systems. These transitional species are endowed with oxygen bridge, which enables the equilibration of electrons in d orbitals of chromium and manganese. This mechanism of oxygen elimination through condensation seems to be general for all the reactions of oxo-compounds of the dsp block connected with evolution of oxygen, both in decomposition of oxides and oxo-salts, and in their reduction with hydrogen or carbon. The formation of crystallographic shear in reduction of such oxides as $TiO_2$, $V_2O_5$, $WO_3$, $MoO_3$, $Nb_2O_5$ and formation of new oxides of complex stoichiometry is just a result of such an elimination of oxygen.

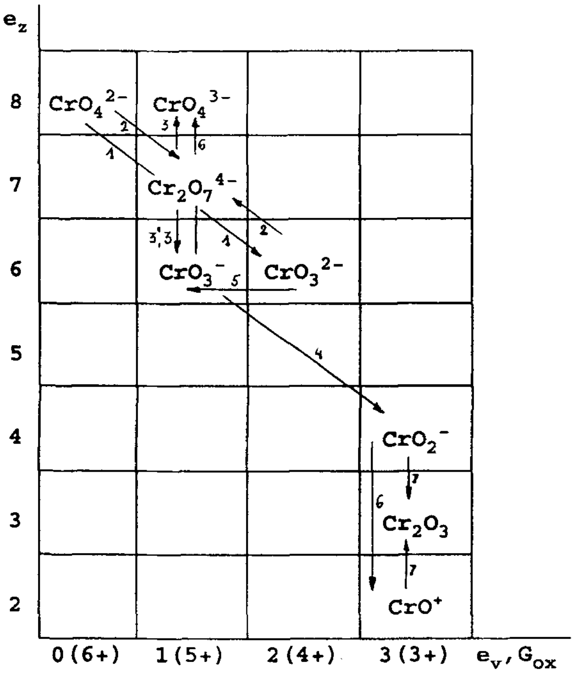


**Fig. 5** Steps in decomposition of anionic sublattice of $CrO_4^{2-}$

Unstable anions $Mn_2O_7^{2-}$ and $Cr_2O_7^{4-}$ undergo further reaction which leads to formation of anions $MnO_4^{2-}$ and $CrO_4^{3-}$ stable in salt systems:

$$Mn_2O_7^{2-} \rightarrow MnO_4^{2-} + MnO_3^{0} \qquad (3)\ \text{Fig. 4}$$

$$Cr_2O_7^{4-} \rightarrow CrO_4^{3-} + CrO_3^{-} \qquad (3)\ \text{Fig. 5}$$

and the unstable species lose oxygen to form anions of the end-products:

$$MnO_3^{0} \rightarrow MnO_2 + O \qquad (4)\ \text{Fig. 4}$$

$$CrO_3^{-} \rightarrow CrO_2^{-} + O \qquad (4)\ \text{Fig. 5}$$

An additional confirmation of the possibility of electron transfer through bridging oxide ligands are the disproportionation reactions effected in aqueous solutions of salts containing the $MnO_4^{2-}$ and $CrO_4^{3-}$ anions, for example $K_2MnO_4$ and $K_3CrO_4$:

$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$$

$$3K_3CrO_4 + 4H_2O \rightarrow 2K_2CrO_4 + K_3[Cr(OH)_6] + 2KOH$$

The $MnO_4^{2-}$ and $CrO_4^{3-}$ ions with acid-base properties similar to those of isostructural ions $CrO_4^{2-}$ and $VO_4^{3-}$ which are stable in aqueous solutions, will hydrolyse in solutions to form anions $HMnO_4^-$ and $HCrO_4^{2-}$. Like the chromate(VI) and vanadate(V) ions, these anions are easily condensed to form $Mn_2O_7^{2-}$ and $Cr_2O_7^{4-}$ ions which undergo a redox disproportionation which consists in transfer of d electrons from one chromium or manganese core to the other one, by means of the oxygen bridge. The final effect in this series of elementary steps is the formation of chromate(VI) and manganate(VII) anions stable in aqueous solutions. The oxo compounds of manganese(V) and chromium(IV) formed in the disproportionation reaction undergo similar transformations which end by stable products given in the balance equations of hydrolysis.

The above-presented decomposition schemes are applicable to decomposition of all anhydrous manganates(VII) and chromates(VI) with cations of weakly acidic properties belonging to the second group in the above-presented classification. These are the basic schemes of decomposition in which the effect of cations does not appear, and their part is reduced to stabilization of the end product phases. The other four groups of chromates(VI) decompose to yield other products and that is the consequence of interaction of the cations with intermediate chromium oxo compounds formed in the course of the decomposition.

The chromates(VI) belonging to the first group contain cations that possess oxidizing properties at increased temperatures. In the presence of reducing substances they are capable of binding electrons and thus they are converted into metal vapors or, in the case of silver, into solid metal phase. After elimination of a part of oxygen from $CrO_4^{2-}$ the strongly reducing $CrO_3^{2-}$ ions will react with the cations to give metal vapors or metallic silver:

$$CrO_3^{2-} + M^+ \rightarrow CrO_3^- + M \qquad \text{(5) Fig. 5}$$

and the $CrO_3^-$ ions, which are weaker reducers, are decomposed to form $CrO_2^-$ (4). For this group of chromates(VI) the schemes of decomposition will pass through the following steps:

$$\begin{array}{cr}
CrO_4^{2-} + 2M^+ \rightarrow CrO_3^{2-} + 2M^+ + O & \text{(1) Fig. 5} \\
CrO_3^{2-} + M^+ \rightarrow CrO_3^- + M & \text{(5) Fig. 5} \\
\underline{CrO_3^{2-} \rightarrow CrO_2^- + O} & \text{(4) Fig. 5} \\
\hline
M_2CrO_4 \rightarrow M + MCrO_2 + O_2 & (\Sigma)
\end{array}$$

In the third group of chromates(VI) with cations $M^{3+}$ the $CrO_2^-$ ions cannot be stabilized in the products since cations belonging to this group do not form such salts. The only two possibilities are: formation of salts containing $CrO_3^{3-}$ sublattice or isolation of $Cr_2O_3$. However, formation of anionic $CrO_3^{3-}$ sublattice would require the presence of species with basic properties stronger than those in $CrO_2^-$, but such species are not present in the reaction system. Thus, only $Cr_2O_3$ may be formed in reaction of $CrO_2^-$ with acidic species, and just such a species is $CrO_3^-$. The steps of decomposition of chromates(VI) belonging to this group may be represented by the following scheme (Fig. 5):

$$3CrO_4^{2-} \rightarrow 3CrO_3^{2-} + 3O \qquad (1)$$

$$3CrO_4^{2-} + 3CrO_3^{2-} \rightarrow 3Cr_2O_7^{4-} \qquad (2)$$

$$3Cr_2O_7^{4-} \rightarrow 3CrO_4^{3-} + 3CrO_3^- \qquad (3)$$

$$2CrO_3^- \rightarrow CrO_2^- + 2O \qquad \text{(4) Fig. 5}$$

$$CrO_3^- + CrO_2^- \rightarrow CrO_4^{3-} + CrO^+ \qquad (6)$$

$$CrO^+ + CrO_2^- \rightarrow Cr_2O_3 \qquad (7)$$

$$6CrO_4^{2-} \rightarrow 4CrO_4^{3-} + Cr_2O_3 + 2.5O_2 \qquad (\Sigma)$$

The fourth group of chromates(VI) with strongly acidic cations decompose with formation of solely $CrO_2^-$ sublattice. The strongly acidic interaction of the cations prevents the formation of $CrO_4^{3-}$ anions during the decomposition. The scheme of decomposition in this group may be represented by the following steps (Fig. 5):

$$CrO_4^{2-} \rightarrow CrO_3^{2-} + O \qquad (1)$$

$$CrO_3^{2-} + CrO_4^{2-} \rightarrow Cr_2O_7^{4-} \qquad (2)$$

$$Cr_2O_7^{4-} + (M^{2+}) \rightarrow 2CrO_3^- + (O^{2-} + M^{2+}) \qquad (3')$$

$$2CrO_3^- \rightarrow 2CrO_2^- + 2O \qquad (4)$$

$$2CrO_4^{2-} \rightarrow 2CrO_2^- + O^{2-} + 1.5O_2 \qquad (\Sigma)$$

At last, in decomposition of chromates(VI) with cations having the strongest acidic nature, such as $Sc^{3+}$ or $ScO^+$, they react with $CrO_2^-$ formed in previous steps to give $Cr_2O_3$ and $Sc_2O_3$.

The above-proposed schemes of stepwise decomposition of manganates(VII) needed a correlation between thermal behaviour of manganese compounds at higher oxidation degrees(VII, VI, V and IV), and in the case of chromates(VI)– between practically all the oxo compounds of chromium. If such schemes are to be reliable it is necessary to correlate them with the course of other types of chemical reactions of oxo compounds of the given element, in addition to thermal decompositions, for example reactions of oxidation, action of acids or bases, etc.

## References

1 A. Górski, Roczniki Chemii., 45 (1971) 1981.
2 A. Górski, Roczniki Chemii., 45 (1971) 2153.
3 A. Górski, Roczniki Chemii., 45 (1971) 2201.
4 A. Górski, Roczniki Chemii., 46 (1972) 127.
5 Z. Gontarz and A. Gorski, Polish J. Chem., 45 (1991) 191.
6 Z. Gontarz, Polish J. Chem., 45 (1991) 217.
7 Z. Gontarz, Polish J. Chem., 45 (1991) 229.
8 Z. Gontarz, Polish J. Chem., 45 (1991) 239.
9 Z. Gontarz, Polish J. Chem., 45 (1991) 711.
10 Z. Gontarz, Polish J. Chem., 45 (1991) 721.
11 Z. Gontarz, Polish J. Chem., 45 (1991) 731.
12 Z. Gontarz, Polish J. Chem., 45 (1991) 743.
13 Z. Gontarz and B. Pisarska, J. Thermal Anal., 36 (1990) 2113.

**Zusammenfassung** — Eine Analyse der thermischen Zersetzung von Manganaten(VII) und Chromaten(VI) der morphologischen Klassifizierung von Gorski wurde benutzt, um typische Schritte der Zersetzung von Oxiden und Oxosalzen der Elemente des dsp-Feldes zu unterscheiden und den Effekt der kationischen Gegenionen auf die Zersetzung von Chromaten(VI) zu bestimmen.