

Method of Determining Radii and Enthalpies of The Formation of Poliatomic Ions

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Abstract

Based on the Born-Haber cycle, a method is proposed for determining the thermochemical radii and enthalpies of the formation of polyatomic ions. In order to be able to compare the values of the enthalpies of the formation of ions and salts, a method is proposed for normalizing these values by relating them not to one mole of a substance, but to an averaged gram atom. The method is approved on vanadium oxide compounds. The values of 22 radii and enthalpies of the formation of polyatomic ions containing vanadium, the energies of the crystal lattices and the enthalpies of formation of 81 vanadate are calculated. The obtained values are compared with the experimental data.

Keywords: Polyatomic Ions, Ion Radii, Born-Haber Cycle, Enthalpy Of Vanadate Formation, Lattice Energy Of Vanadates.

1. Introduction

Among the methods of approximate calculation of the thermodynamic characteristics of substances, a special place is occupied by methods based on the concept of conditional thermochemical radii, by which are meant the radii of hypothetical spherical ions that replace the ions in an energy-independent manner in the crystal lattice of the salt [1]. If we equate the expressions for the energy of the crystal lattice U obtained from the Born-Haber cycle [1 – 3]

$$U = -\Delta_f H^0 + \Delta_f H_k^0 + \Delta_f H_a^0$$

and the Kapustinskii formula [4]

$$U = 1201,64 \frac{\sum n Z_k Z_a}{r_k + r_a} \left(1 - \frac{0,345}{r_k + r_a} \right),$$

we obtain the equation

$$U = 1201,64 \frac{\sum n Z_k Z_a}{r_k + r_a} \left(1 - \frac{0,345}{r_k + r_a} \right) = -\Delta_f H^0 + \Delta_f H_k^0 + \Delta_f H_a^0 \quad \text{kJ/mol}, \quad (1)$$

where n is the number of ions forming the salt molecule; Z_k, Z_a, r_k, r_a – charges and radii of the cation and anion and $\Delta_f H_k^0, \Delta_f H_a^0, \Delta_f H^0$ – the enthalpy of formation of the cation, anion and salt, respectively. Read more about the theory of this method can be found in the review of J. Sherman [5]. The solution of the system of such equations makes it possible to estimate the enthalpies of the formation of the corresponding salts. In the case of ions, in form close to spherical, there is no difference between thermochemical and crystallographic radii [1]. If, however, the shape of the ions differs significantly from the spherical, the thermochemical radii can be found from equation (1). The enthalpy of formation of monatomic cations is equal to:

$$\Delta_f H_a^0 = \Delta H^0 + I, \quad (2)$$

where $I = \sum I_i$ is the total ionization potential, ΔH^0 is the enthalpy of atom formation. For substances that are in standard conditions in the condensed state and evaporate in the form of monatomic gases, the enthalpy of

formation is equal to their enthalpy of sublimation [6]. Similarly, using the dissociation energy and electron affinity, the corresponding enthalpy values of the formation of monatomic ions are calculated. The reference [7] gives the heats of formation as a function of the temperature of cations with an oxidation state of +1 and there is a principal possibility of having such data for the heats of ion formation with any degree of oxidation. From this it follows that systems of equations of the form (1), in principle, can allow one to find the dependence of the enthalpies of formation of complex ions and their thermochemical radii on temperature and pressure, which in turn allows one to find the enthalpy of formation of any ionic compounds under different conditions, their heat capacities, entropies, and thermodynamic functions. It is necessary to pay special attention to the existence of an ion H^+ , whose thermochemical radius is independent of external conditions and equal to zero. This simplifies the task. The main advantage of the discovered method for estimating thermodynamic potentials, and, at the same time, the direction of chemical reactions, is that after preliminary establishment of a system of dependences of the thermochemical radii and heats of ion formation from external conditions, primarily temperature and pressure, the main thermodynamic characteristics of the substance can be simply calculated. At the same time, the corresponding quantities can be obtained in another way only experimentally or by comparative methods of calculation [2].

The purpose of this work is to find a method for calculating the thermochemical radii of polyatomic ions and, using the obtained radii, determine the enthalpy of formation and the energy of crystal lattices of a number of inorganic compounds using the Born-Haber cycle. As such, selected vanadates of various metals. This choice was made on the basis of the fact that they are relatively fully investigated and many chemical compounds with varying degrees of vanadium oxidation, among them oxide vanadium bronzes, are known among them.

2. Theory of The Method

When trying to use the proposed method, complications also arise in the definition of a complex polyatomic ion, since the values of the thermochemical characteristics of the ion must be related to its composition, which can be normalized in various ways. The existence of a linear dependence of the thermodynamic characteristics of substances and processes on the formula indices and the mass fractions of the corresponding components indicates that the determining factor in the estimation of these quantities must be extensive. The thermodynamic data is usually related to one mole of the substance. But the formula indexes of elements determine only the relationships between these elements, which makes the molar mass of matter relative. In order for the thermodynamic characteristics of substances to be comparable to each other, the molar masses of any substances must be represented in some uniform way. Since the values of the thermodynamic characteristics of individual substances and reactions between them are determined not only by the types of chemical bonds between atoms and species of the atoms themselves, of which these substances are composed, but also by their total quantity, the formulas of any substances for comparative evaluation should be recorded in such a way that the total quantity atoms in the formula of any substance was the same. This is achieved by the fact that the sum of the formula indices is taken to be equal to the same constant. It is most convenient to choose one as such a constant. This means that the values of the thermodynamic characteristics will be attributed to the averaged gram atom of the substance. The normalization extends to changes in thermodynamic potentials in the course of chemical reactions. To do this, the mass fractions or stoichiometric coefficients of the reaction components are selected in such a way that their sum is also equal to unity. The use of normalized thermodynamic characteristics makes it possible to give a comparative evaluation of their changes in the process of even such reactions, the initial components in which cannot even contain common chemical elements. With respect to polyatomic ions, what has been said convinces us of the need to relate the characteristics of the ions to their composition. For example, oxygen-containing ions of the type $A_p O_m^{pa-2m}$, where $(pa - 2m)$ – the charge of an ion, a – the degree of oxidation of a chemical element A, is conveniently written in the form AO_n^{a-2n} , here $n = \frac{m}{p}$, then the dependence of the thermodynamic characteristics from n , and the corresponding reduced values, referred to the number of bonds of the central atom with oxygen or the total number of atoms in the ion composition, It makes it easier to identify the patterns that are possible for the characteristics analyzed. Thus, it is natural to expect that the enthalpy of formation $\Delta_f H(AO_n^{a-2n})$ minus the enthalpies of formation of

oxygen ions and a central atom, referred to the number of $A - O$ bonds, will be inversely proportional n , since the introduction of additional oxygen ions into the composition of the complex ion with increasing n will give an ever smaller gain in energy. This is due to the increasing repulsive forces between the oxygen ions in the complex ion. At some maximum value, there will be no gain in energy at all. Such a dependence can be useful in determining the enthalpy of formation of complex ions.

As for the thermochemical radii of complex ions, it is natural to assume that they must possess all the properties of the geometric radii of certain spherical volumes. Since at small such volumes must be very different from spherical, this forces the thermochemical radii to be considered conditional. However, as a consequence of our assumption about the conditional sphericity of complex ions when the content of any atoms in the ion composition increases, the structure of the ion, in the thermochemical sense, should not take place. From this it follows that the volume of a complex ion, starting with some neutral state with zero charge, when additional elementary ions are added to its composition, must increase exactly by the volume of these ions. The conditional thermochemical radius of the resulting ion, given its structurelessness, must be the radius of a sphere whose volume is equivalent to the volume of a new complex ion. For this reason, in contrast to the crystallochemical radii of monatomic ions, which are considered to be elastic incompressible spheres, the conditional thermochemical radii of polyatomic ions, on the contrary, should be perceived as inelastic spherical formations. This makes it possible to estimate the thermochemical radius of any complex ion if any radii of at least two ions of the same type are already known in some way, but with a different content of one of the types of atoms that make up the complex ion.

Let, for example, it be required to find the radius r_n of an ion AO_n^{a-2n} if the radii r_m and r_p ions AO_m^{a-2m} and AO_p^{a-2p} are, accordingly. Each ion of radius r_p is combined with α ions of radius r_m . As a result, the composition of the formed ion will contain as many oxygen atoms as possible, which is the arithmetic average of their contents

$$n = \frac{p + \alpha m}{1 + \alpha} \quad (3)$$

in the initial ions with radii r_m and r_p . The volume of the complex ion that is formed will also be equal to the average arithmetic volume of the initial ions

$$\frac{4}{3}\pi r_n^3 = \frac{4\pi}{3(1+\alpha)}(r_p^3 + \alpha r_m^3) \quad (4)$$

Substituting the value α from (3) into (4), we obtain a formula for the radius of a polyatomic ion containing n oxygen atoms:

$$r_n = \sqrt[3]{\frac{(n-m)r_p^3 + (p-n)r_m^3}{p-m}} \quad (5)$$

The enthalpy of formation of polyatomic ions, as already mentioned, is a solution of a system of equations of the type (1).

3. Application of The Method

We show how the proposed method of determining thermochemical radii, the enthalpy of polyatomic ions, and the enthalpies of formation of various salts on the example of complex oxide compounds based on vanadium work.

In [2], the thermochemical radii of ions VO_3^- and VO_4^{3-} were estimated from the data of the structure of vanadates of alkaline, alkaline-earth, and rare-earth elements. To determine the radius of the orthovanadate ion $r_{VO_4^{3-}}$, the parameters of the crystal lattices of orthovanadates, orthophosphates, and orthoarsenates of rare-

earth elements were used [8]. The radii of orthophosphate $r_{PO_4}^{3-} = 2,38 \text{ \AA}$ and orthoarsenate $r_{AsO_4}^{3-} = 2,48 \text{ \AA}$ ions were taken from the monograph [1]. It was noted that for orthophosphates and orthoarsenates, the ratio of the sum of the parameters of the crystal lattice of these compounds, regardless of the type of the rare-earth element, to the doubled sum of the radii of the cation and anion is 1.99. Considering the isostraturation of orthovanadates of orthophosphates and orthoarsenates of rare-earth elements, it was concluded that the same dependence should be fulfilled for orthovanadates, from where the radius of the orthovanadate ion $r_{VO_4}^{3-} = 2,48 \text{ \AA}$ was found.

Considering the sum of the parameters of the crystal lattice as a multiple of the sum of the radii of the cation and anion, the radius of the metavanadate ion was found. If the number of ions per unit cell edge is not known, then the degree of multiplicity of the sum of the cell parameters to the sum of the radii of the cation and anion can be found in the following way. A graphical dependence of the radii, in this case, of oxygen-containing ions, the values of which are available in reference books or original works, for example, in [1] on the radius of the ion of the main element, is constructed. According to the obtained dependence there is an assumed interval in which the value of the radius of the desired ion must be located. For the metavanadate ion, this interval will be $1.7 - 1.8 \text{ \AA}$. The degree of multiplicity will be equal to the nearest integer taken from the ratio of the sum of the parameters to the sum of the radii of the cation and the approximate value of the radius of the anion.

According to the data of [9], the distances $V - O$ in the potassium metavanadate are 1.81; 1.81; 1.66; 1.65 Å, in ammonium metavanadate, respectively, 1.80; 1.80; 1.65; 1.67 Å. The averaging of these distances gives a close value of 1.73 Å.

Having solved the system of equations of the type (1) for sodium and calcium metavanadates, the heat of formation of which $\Delta_f H_{298}^0$ are 1150.95 and 2330.79 kJ/mol, respectively, [10, 11], and the heat of formation of sodium and calcium cations is 602.48 and 18894.95 kJ/mol, respectively, [1] using radial values from the reference book [12], we find the heat of formation of the desired ions $\Delta_f H_{298}^0(VO_3^-) = -975 \text{ kJ/mol}$. Using the heat of formation of sodium orthovanadate (1762.65 kJ/mol [10]) and the heat of formation of the gaseous sodium ion (602.48 kJ/mol [1]), using equation (1), we determine the heat of formation of the gaseous ion of orthovanadate

$$\Delta_f H_{298}^0(VO_4^{3-}) = -203,06 \text{ kJ/mol}$$

To date, the heat of formation for a relatively large number of vanadates has been determined experimentally, the values of which are collected in the monograph [13]. These data make it possible to estimate the thermochemical radii and enthalpies of vanadate formation with the help of equation (1) more reliably. First of all, such work was carried out for meta- and orthovanadates. For the most reliable, the averaged results obtained from the experimental data for vanadates with an equal number of cations and anions in their composition were taken. As a result, the optimal radii and ions formation enthalpies VO_3^- were found equal to 1.78 Å; -979.1 kJ/mol and VO_4^{3-} equal to 2.48 Å; 216.4 kJ/mol, respectively. Taking the obtained values of the radii of meta and orthovanadate as a basis and substituting these values into formula (5), we obtain the following formula for the radii of negatively charged vanadate ions:

$$r(VO_n^{5-2n}) = \sqrt[3]{9,61n - 23,19} \text{ \AA}, \quad (6)$$

where $n \geq 2,5$. It follows from formula (6) that the conventional thermochemical radius of vanadium in the oxidation state +5 ($n = 0$) is 0.4 Å, and the groupings $r_{VO_{2,5}} = 0,94 \text{ \AA}$. Having chosen these values as r_m and r_p , from the formula (5) we find an analogous expression for positively charged vanadium oxide ions (such as VO^{3+}, VO_2^+ and other).

$$r(VO_n^{5-2n}) = \sqrt[3]{0,307n - 0,064} \text{ \AA}, \quad (7)$$

where $0 \leq n \leq 2,5$.

In Fig. 1 shows the curve of the dependence of the radii of vanadate ions $r(\text{VO}_n^{5-2n})$ on the number of oxygen ions n per one vanadium atom, calculated from formulas (6, 7). It can be seen from this figure that this curve represents two cubic parabolas intersecting at a value $n = 2,5$, that corresponds to a zero charge of the ion and corresponds to pure vanadium pentoxide V_2O_5 .

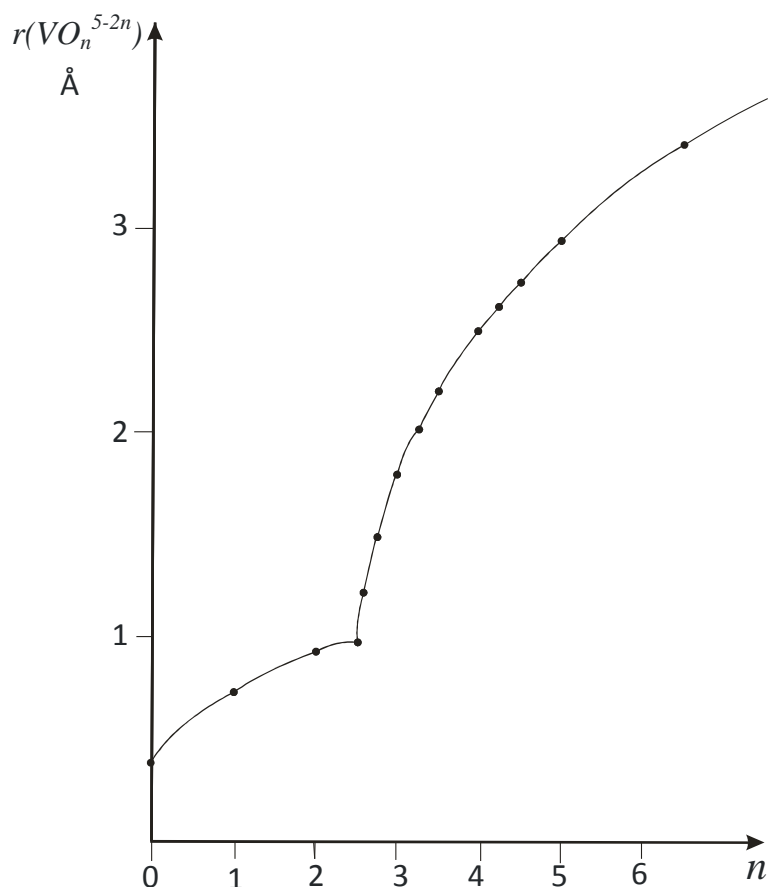


Fig. 1. Dependence of the radius of vanadate ions on the oxygen content in them.

To determine the dependence of the heat of formation of vanadate ions on n , it was taken into account that the value $\Delta_f H_{298}^0(\text{V}^{5+})$ calculated by formula (2) with the help of the data given in the reference books [6, 14] is 16324 kJ/mol ; $\Delta_f H_{298}^0(\text{VO}^{3+}) = 151,46 \text{ kJ/mol}$ and $\Delta_f H_{298}^0(\text{VO}_2^+) = -233,05 \text{ kJ/mol}$ [6]; $\Delta_f H_{298}^0(\text{VO}_{2,5})$ is equal to half the value of the enthalpy of formation V_2O_5 and amounts to 775.5 kJ/mol ; the value $\Delta_f H_{298}^0(\text{VO}_{3,5}^{2-}) = 776 \text{ kJ/mol}$ is obtained with the aid of equation (1) as the arithmetic average enthalpy of the formation of the pyrvanadate ion for alkaline earth metals.

Taking into account the aforementioned values of the heats of formation of the meta- and orthovanadate ions, and also, according to the data [1], the formation enthalpy of the oxygen ion $\Delta_f H_{298}^0(\text{O}^{2-}) = 875,71 \text{ kJ/mol}$ it is easy to see that the quantity

$$\Delta_f H_{298}^0(\text{V}^{5+} - \text{O}^{2-}) = \frac{1}{n} [\Delta_f H_{298}^0(\text{VO}_n^{5-2n}) - \Delta_f H_{298}^0(\text{V}^{5+}) - n\Delta_f H_{298}^0(\text{O}^{2-})] \quad (8)$$

linearly depends on $1/n$ (Fig. 2).

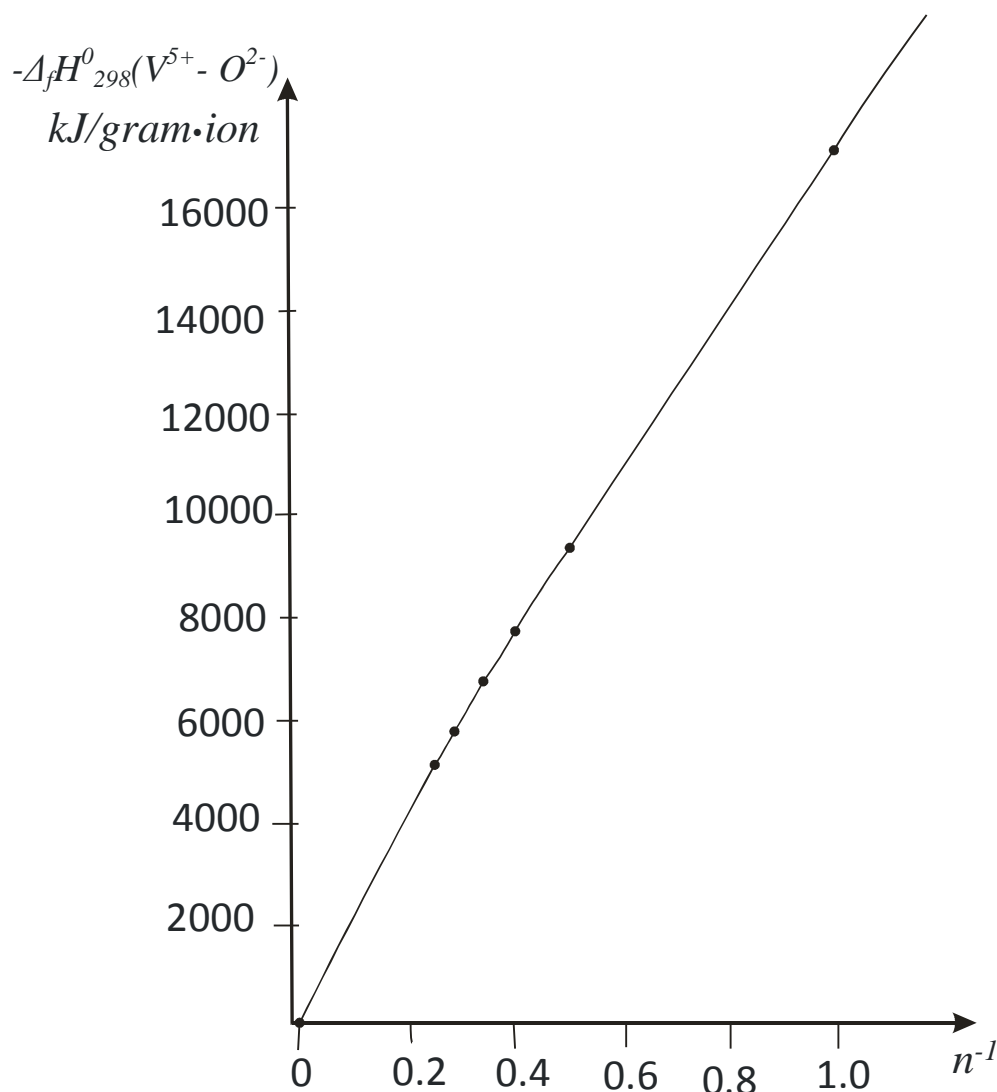


Fig. 2. Dependence of the enthalpy of formation bond $V^{5+} - O^{2-}$ of the anion VO_n^{5-2n} on the reciprocal of the relative oxygen content in the anion n^{-1} .

This indicates that the given dependence can be extrapolated to those values n for which the corresponding quantities $\Delta_f H_{298}^0(VO_n^{5-2n})$ are not yet known. However, in practice it turned out that the available heats of formation on one hand are not accurate enough, and the revealed dependence is not strictly linear. In this connection, the interpolation Lagrange polynomial was constructed for the dependence of the enthalpies of formation of vanadate ions on n (kJ/mol):

$$\Delta_f H_{298}^0(VO_n^{5-2n}) = -28195n^7 + 591,375n^6 - 5035,91n^5 - 56872n^3 + 79596n^2 - 56981n + 16324,7 \quad (9)$$

Table 1. Values of conditional thermochemical radii and enthalpies of formation of ions VO_n^{5-2n} (kJ/gram-ion)

n	r_n Å	$\Delta_f H_{298}^0(VO_n^{5-2n})$ kJ/mol	$\Delta_f H_{298}^0(VO_n^{5-2n})$ kJ/mol

		(calculated by the formulas 6, 7)	(according to literary data)
0	0.40	16324.7	
0.50	0.60	837.9	
1.00	0.72	151.4	151.46 [6]
1.50	0.81	–	
2.00	0.88	–233.0	–233.05 [6]
2.50	0.94	–774.5	–775.5 [13]
2.56	1.12	–818.3	
2.58	1,17	–833.9	
2.60	1.22	–849.0	
2.62	1.27	–864.7	
2.67	1.35	–893.6	
2.75	1.48	–926.6	
2.80	1.55	–947.0	
3.00	1.78	–979.1	
3.25	2.00	–943.2	
3.33	2.07	–889.9	
3,50	2,19	–763,5	
4.00	2.48	216.4	202.9 [6]
4.25	2.60	≈550	
4.50	2.72	≈890	
5.00	2.92	≈1560	
6.50	3.40	≈3360	

Table 2. Crystal lattice energies and enthalpies formation of vanadates.

Vanadat	U	$-\Delta_f H_{298}^0$	
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	$\frac{kJ}{mol}$	$\frac{kJ}{g \cdot atom}$	Calculated by the equation (1)		According to [13]	Divergence at %
			$\frac{kJ}{mol}$	$\frac{kJ}{g \cdot atom}$	$\frac{kJ}{mol}$	
$Li_2V_{17}O_{43,5}$	1230.3	19.68	13911	222.58		
$LiV_6O_{15,5}$	616.2	28.01	4939.9	219.55		
LiV_3O_8	668.2	55.69	2669.3	222.45		
$LiVO_3$	839.9	167.98	1139.3	227.87	1123*	1.4
Li_3VO_4	4065.0	508.12	1809.6	226.20	2005	9.7
$Na_2V_{17}O_{43,5}$	1090.3	17.44	13911	22,58		
$NaV_6O_{15,5}$	574.4	24.33	4947.2	219.88		
NaV_3O_8	597.5	49.79	2674.7	222.89		
$NaVO_3$	761.9	152.38	1137.4	227.48	1147	0.9
$Na_5V_3O_{10}$	4640.2	257.79	4292.0	238.44		
$Na_4V_2O_7$	4053.7	311.83	3166.4	243.57	2919.2	7,8
Na_3VO_4	3752.0	469.00	1724.9	215.61	1758.1	1.9
$KV_6O_{15,5}$	483.2	21.47	4978.5	221.27		
KV_5O_{13}	489.0	25.74	4225.9	222.42		
$KV_4O_{10,5}$	501.1	32.33	3451.8	222.70		
KV_3O_8	531.3	44.27	2704.0	225.33	2759.1	2
$K_3V_5O_{14}$	1762.8	80.13	4973.5	226.07	5068.9	1.9
KVO_3	687.0	137.4	1158.0	231.60	1167.3	0.8
$K_5V_3O_{10}$	4217.2	234.29	4346.4	241.47		
$K_4V_2O_7$	3695.0	284.23	3189.6	245.36	3022,3	5.2
K_3VO_4	3442.0	430.25	1701.3	212.66	1815.4	6.3
RbV_5O_{13}	464.4	24.43	4225.6	222.40		

$RbV_4O_{10,5}$	476.2	30.72	3451.2	202.66		
RbV_3O_8	505.5	42.12	2702.5	225.21	2808.0	3.8
$Rb_3V_5O_{14}$	1682.0	76.45	4965.5	225.70	5102.8	2.7
$RbVO_3$	657.4	131.4	1152.7	230.53	1147.4	0.5
$Rb_5V_3O_{10}$	4048.1	224.9	4248.6	236.03		
$Rb_4V_2O_7$	3551.0	273.16	3142.7	241.74	2963.7	5.7
Rb_3VO_4	3316.6	414.57	1648.7	206.09	1789.0	7.8
CsV_3O_8	482.1	40.17	2711.1	225.92	2769.6	2.1
$Cs_2V_4O_{11}$	1024.8	60.28	3827.6	225.15	3918.0	2.3
$CsVO_3$	630.2	126.04	1157.5	231.50	1148.2	0.8
$Cs_5V_3O_{10}$	3891.9	216.22	3792.5	210.69		
$Cs_4V_2O_7$	3417.8	262.90	3137.5	241.34	2970.8	5.3
Cs_3VO_4	3199.8	399.98	1627.9	203.49	1814.0	10.3
$NH_4V_3O_8$	514.9	42.91	2586.9	215.58	2612.5*	1.0
$(NH_4)_2V_4O_{11}$	1091.9	64.23	3580.8	210.64	3678.4*	2.7
NH_4VO_3	668.2	133.64	1038.5	207.71	1053.1	1.4
MgV_2O_6	2469.4	274.37	2092.5	232.50	2200.3	4.9
$Mg_2V_2O_7$	5806.4	527.85	2663.2	242.11	2835.5	6.1
$Mg_3V_2O_8$	9995.9	768.92	2557.7	196.75	3464.3	26.2
CaV_2O_6	2243.9	249.32	2288.4	254.27	2328.2	1.7
$Ca_2V_2O_7$	5331.2	484.65	3030.8	275.53	3083.2	1.7
$Ca_3V_2O_8$	9237.6	710.58	3063.7	235.67	3777.9	18.9
$Ca_7V_4O_{17}$	19641	701.50	4033.5	144.05		
$Ca_4V_2O_9$	13932	928.84	4499.7	299.98	4570*	1.5
$Ca_5V_2O_{10}$	25403	1494.3	12712	747.79		
SrV_2O_6	2139.3	237.7	2320.1	257.79	2350*	1.3

$Sr_2V_2O_7$	5107.7	464.34	3139.8	285.44	3151.3	0.4
$Sr_3V_2O_8$	8877.7	682.90	3112.6	239.43	3873.0	19.6
$Sr_4V_2O_9$	13419	894.6	4531.3	302.09	4700*	3.6
BaV_2O_6	2032.5	225.83	2339.2	259.91	2320*	0.8
$Ba_2V_2O_7$	4877.3	443.40	3101.3	281.93	3115.0	0.4
$Ba_3V_2O_8$	8504.5	654.19	3117.2	239.78	3861.4	19.3
$Ba_4V_2O_9$	12884	858.95	4500.2	300.01		
CuV_2O_6	2420.8	268.98	1337.7	148.63	1744*	23.3
$Cu_2V_2O_7$	5704.8	518.62	1149.1	104.47	1930*	40.5
MnV_2O_6	2336.5	259.61	1783.5	198.17	1998.7	10.8
$Mn_2V_2O_7$	5527.4	502.49	2032.0	184.73	2480*	18.1
ZnV_2O_6	2397.3	266.37	1584.9	176.10	1910*	17.0
$Mn_2V_2O_7$	5655.4	514.13	1641.3	149.21	2287.1	28.2
CdV_2O_6	2278.7	253.19	1625.6	180.62	1840*	11.7
$Cd_2V_2O_7$	5405.0	491.36	1709.4	155.40	2137.4	20.0
NiV_2O_6	2469.4	274.38	1509.7	167.74	1821*	17.1
$Ni_2V_2O_7$	5806.4	527.86	1497.5	136.13	2080*	28.0
CoV_2O_6	2436.8	270.76	1561.6	173.51	1862*	16.2
$Co_2V_2O_7$	5978.3	543.48	1838.4	167.13	2150*	14.5
PbV_2O_6	2102.5	233.61	1699.4	188.82	1820*	6.6
$Pb_2V_2O_7$	5028.5	457.14	1832.9	166.63	2131.8	14.0
YVO_4	5462.5	940.41	1047.4	174.57		
$LaVO_4$	5542.5	923.75	1401.0	233.50		
$SmVO_4$	5462.5	940.41	1739.2	289.86		
$EuVO_4$	5462.5	940.41	1749.9	291.66		
$GdVO_4$	5686.5	947.74	1544.7	257.45	1788	13.6

<i>TbVO₄</i>	5761.2	960.20	1791.3	298.54	1796	0.3
<i>DyVO₄</i>	5776.4	962.74	1815.0	302.51	1804	0.6
<i>HoVO₄</i>	5807.0	967.84	1830.2	305.04	1800	1.7
<i>ErVO₄</i>	5822.5	970.42	1792.9	298.80	1809	0.9
<i>TuVO₄</i>	5822.5	970.42	1829.5	304.91	1779	2.7
<i>YbVO₄</i>	5884.9	980.83	1933.5	322.26	1754	9.2
<i>LuVO₄</i>	5900.8	983.47	1627.8	271.30	1800	9.6

* Evaluated by comparative calculation methods (extrapolation and interpolation) [2].

Formula (9) makes it possible to calculate the enthalpies of formation of vanadate ions when the $0 \leq n \leq 4$. Reason for this restriction was the presence of an extremum of function (9) with $n \approx 5$. Accordingly, the values of enthalpies from $n > 4$ are estimated approximately, assuming their linear dependence on the content of oxygen atoms in the composition of these ions. Calculated by formulas (6, 7), the values of the conditional thermochemical radii and enthalpies of formation of vanadium-based ions according to the formula (9) are presented in Table. 1, 2.

The radii of oxide, based on vanadium, ions increase with increasing oxygen content in the ion composition. This dependence undergoes a fracture at, which corresponds to vanadium pentoxide. From tab. 1 shows that the dependence of the values of the enthalpies of formation of ions on the content of oxygen in them experience an extremum at $n = 3$, which corresponds to the ion of metavanadate.

The crystal lattice energies and the formation enthalpies of vanadates, calculated using equation (1), are presented in Table. 2. For calculation, the crystal-chemical radii of the cations from [14 – 16] and the data in Table 2 were used. 1. From table. 2 that the enthalpies of formation of vanadates, assigned to one prayer substance, are difficult to compare between themselves. At the same time, the values normalized to the gram atom of a substance easily allow this. For the enthalpies of formation of vanadates, as a rule, with a decrease in the content of vanadium in the composition of vanadates, an increase in the values of enthalpies is observed, and after a certain maximum is reached a decrease. So, for alkali and alkaline earth metals, pyrovanadates have such an extreme value. The average error of the method for determining the heat of formation of vanadates, calculated from the degree of discrepancy between the calculated values and the experimental values, is. Such a comparatively large average error of the method is caused by anomalously large discrepancies for pyro- and ortho-vanadates of divalent metals, which requires an appropriate correction of the Kapustinsky formula.

Conclusion

Based on the fact that thermochemical radii of polyatomic ions should have all the properties of the geometrical radii of some spherical volumes, with an increase in the content of any atoms in the ion, the volume of the complex ion, starting with some neutral state with zero charge, should be added to its composition increase by exactly the volume of these ions. The conditional thermochemical radius of the resulting ion should be equal to the radius of the sphere, the volume of which is equivalent to the volume of the new complex ion. For this reason, in contrast to the crystal-chemical radii of monatomic ions, which are considered elastic incompressible balls, conventional thermochemical radii of polyatomic ions, on the contrary, should be perceived as inelastic spherical formations. This makes it possible to estimate the thermochemical radius of any polyatomic ion, if the

radii of at least two ions of the same type, but with a different content of one of the type of atoms that make up the complex ion, are already known in any way. Knowledge of the radii of polyatomic ions allows using the Born-Haber cycle to calculate the enthalpy and energy of crystal lattices of compounds of various classes.

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