

NEGATIVE IONS VO_2^- , VO_3^- , V_2O_5^- , V_3O_8^- , AND $\text{V}_4\text{O}_{10}^-$

IN THE VAPORS OF VANADIUM OXIDES.

DETERMINING ENTHALPIES OF FORMATION FROM EQUILIBRIUM CONSTANTS

E.B. Rudnyi, E.A. Kaibicheva, L.N. Sidorov

Department of Chemistry, Moscow State University,

Moscow 119899, Russia

Short title:

"ENTHALPIES OF FORMATION FROM EQUILIBRIUM CONSTANTS"

Negative ions VO_2^- , VO_3^- , V_2O_5^- , V_3O_8^- , and $\text{V}_4\text{O}_{10}^-$ were found in the vapors of vanadium oxide at 1200 to 1500 K. Equilibrium constants of six reactions with the participation of these ions were estimated. The reactions were chosen in such a manner that the equilibrium constants were non-correlated with each other. Joint processing of the equilibrium constants, which may be named the mixed Second and Third Law treatment, produced the enthalpies of formation of the negative ions, and electron affinities were determined: $\text{EA}(\text{VO}_2) = (223 \pm 20) \text{ kJ} \cdot \text{mol}^{-1}$, $\text{EA}(\text{V}_4\text{O}_{10}) = (401 \pm 61) \text{ kJ} \cdot \text{mol}^{-1}$. The use of vanadium-containing negative ions to measure the activities of vanadium oxide and the oxygen partial pressure has been discussed.

1. Introduction

Negative ions, which are in equilibrium with a condensed phase, exist in vapors of some inorganic compounds at temperatures over 1000 K. ⁽¹⁾ Their presence is due to high electron

affinity of neutral molecules being vaporized or low work function of the surface. In case the concentration of negative ions were not measurable it could be enhanced by adding a small amount of an easily-ionized substance. For example, the admixture of potassium chromate to iron, cobalt, and nickel oxides allowed a measurable concentration of negative ions FeO_2^- , CoO_2^- , and NiO_2^- to arrive at 1400 K. (2,3)

Negative ions in the vapors of vanadium oxide have been investigated in the present work. Ions VO_2^- , VO_3^- , V_2O_5^- , V_3O_8^- , and $\text{V}_4\text{O}_{10}^-$ have been found. Presence so many stable vanadium-containing negative ions in large quantities was a full but pleasant surprise.

Ions VO_2^- and VO_3^- have been observed earlier in secondary-ion mass spectrometry (SIMS) studies of vanadium surface covered by oxygen. (4-8) Ramondo et al (9) carried out ab initio calculation for ion VO_3^- . Thermodynamics of negative oxygen-containing ions of vanadium is unknown.

Measuring equilibrium constants with the participation of negative ions allows such their thermodynamic quantities as the enthalpy of formation and the electron affinity to obtain. If there were only one ion with unknown enthalpy of formation in reactions under study a calculation would be trivial. In common case the task is transformed to solving a system of linear equations. We described earlier the procedure to treat equilibrium constants of a set of reactions by the Third Law approach. (10,11) In this work the procedure has been extended to the case of the mixed approach based on both of the Second and Third Law.

After estimating thermodynamics of negative ions, which exist in the vapors of inorganic compounds, one can use them to

determine partial pressures of neutral molecules and activities of condensed phases. Such a method is analogous to estimating the oxygen pressure by measuring the ratio of the partial pressures of CO and CO₂, or H₂ and H₂O. Examples of applying oxygen-containing negative ions to determining the oxygen partial pressure and the activities of sodium and potassium oxides are given elsewhere. (12) The discovery of negative ions in the vapors of vanadium oxide let us suggest the new method of estimating the activities of vanadium oxides and the partial oxygen pressure.

2. Experimental

This work was performed on a magnet mass spectrometer, model MKh-1303 (Electron, Sumy, Ukraine) (60°, 200 mm), adapted to study (ion + molecule) equilibria. A platinum effusion chamber (diameter 12 mm, height 12 mm) was used with (0.5 to 1.2 mm) effusion orifice. The temperature was measured with a {platinum to (platinum + 10 mass per cent of rhodium)} thermocouple, the accuracy being ±4 K. Ionic currents were measured with a channel electron multiplier model VEU-6. The substances Cr₂O₃, K₂CrO₄, and CoO of chemical grade purity were used. The oxide V₃O₅ was synthesized at our Department of Chemistry and its X-ray analysis didn't show presence of other vanadium oxides.

Another vanadium oxide can be used, our choice was merely due to V₃O₅ being under hand. Mass spectrometry studies (13-17) have shown that higher vanadium oxides decomposed to nonstoichiometric V₂O_{3+x} at high temperatures over 1800 K. In our experiments, where temperatures were lower than 1500 K, X-ray analysis revealed that V₃O₅ didn't decomposed even after several hours of heating. This can be explained by the fact

that the partial oxygen pressure over V_3O_5 is not high enough at our temperatures.

The systems under study and the mass spectra observed are presented in Table 1. Note that the ions were formed inside the effusion cell because of thermal, surface, or self-ionization. Ion $VCrO_6^-$ besides ions presented was in experiments 4 to 6 and ions $V_3O_8^-$ and $V_4O_{10}^-$ were in experiment 6.

A small amount of potassium chromate was added to the mixtures in experiments 1 and 4 to 6. We wanted the concentration of negative ions enhanced as it was in the previous works. (2,3) Yet the concentration of negative ions VO_3^- , $V_2O_5^-$, $V_3O_8^-$, and $V_4O_{10}^-$ happened to be measurable without any admixture to our samples.

To determine the enthalpies of formation of vanadium-containing ions it was necessary to include ions with known enthalpies of formation into equilibrium constants being measured. As such negative ions, CrO_3^- and CrO_4^- were employed. The measurable concentrations of all required ions could be obtained while the mixture comprising chromium oxide mainly was investigated in experiments 4 and 5.

The mixture with cobalt oxide was studied in experiment 6. The enthalpy of formation of CoO_2^- was estimated by us in reference 2. Thus the data of experiment 6 permits checking reliability of the obtained results.

The experiment was planned in such a manner that the several temperatures were chosen. One of them was set and several mass spectra were taken. Later on, using random numbers we went to another temperature and made measurements there. After the series of measurements at other temperatures the run was repeated again at the previous temperature.

The ratio of the partial pressures of ions was calculated from measured ion currents as follows

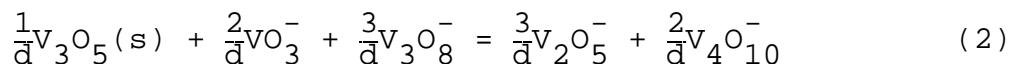
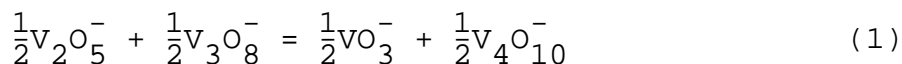
$$\frac{p(A^-)}{p(B^-)} = \frac{I(A^-)}{I(B^-)} \left\{ \frac{M(A^-)}{M(B^-)} \right\}^{1/2} \frac{\gamma(B^-)}{\gamma(A^-)} \frac{i(B^-)}{i(A^-)}$$

where I is an ion current measured with the multiplier, M is the mass of the ion, γ is the multiplier gain, and i is the isotope abundance. The multiplier gain is assumed to be inversely proportional to the square root of ion mass.

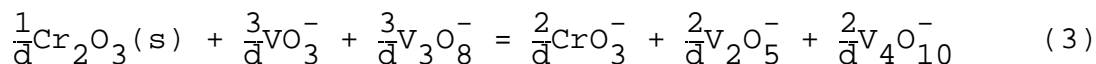
3. Computing equilibrium constants

Our goal was to infer thermodynamics of negative ions VO_2^- , VO_3^- , $V_2O_5^-$, $V_3O_8^-$, and $V_4O_{10}^-$ from the ion currents measured. Equilibrium between the negative ions and the condensed phase has been assumed in this way. We will discuss whether the assumption is trustworthy later on.

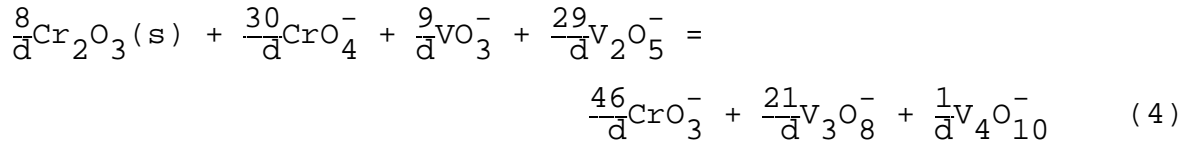
That there are many ions in the vapors of the mixtures under study allows choosing different sets of reactions to describe an equilibrium state. All of them are equivalent since equilibrium state does not depend on the path to reach it. So while selecting the set of reactions (1) to (6) we took into consideration only convenience (see below) and the mechanism of ion formation are not displayed by any means.



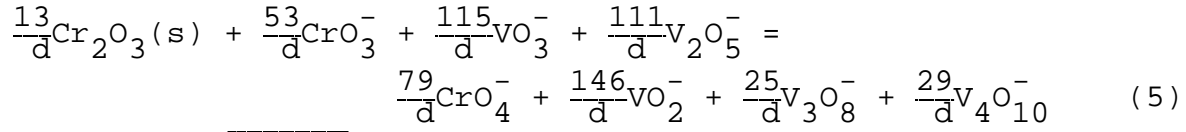
where $d = \sqrt{26}$



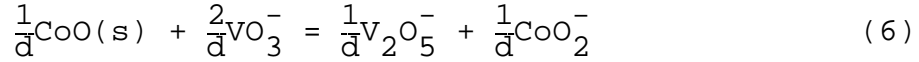
where $d = \sqrt{30}$



where $d = \sqrt{4380}$



where $d = \sqrt{57378}$



where $d = \sqrt{6}$

The equilibrium constants of reactions (1) and (2) were obtained from experiments 1, 2, and 3, the equilibrium constants of reactions (1), (3), (4), and (5) were from experiments 4 and 5, and the equilibrium constants of reaction (6) were from experiment 6. The activities of the condensed phases (V_3O_5 in experiment 1 to 3, Cr_2O_3 in experiment 4 and 5, and CoO in experiment 6) were equated to one. It has been supposed that the admixtures should not change the activity of the chief ingredient in large extent.

The equilibrium constants of reactions 1 to 6 were computed as follows

$$\ln K^{\circ}(1) = \frac{1}{2} \{ \ln I(\text{VO}_3^-) + \ln I(\text{V}_4\text{O}_{10}^-) - \ln I(\text{V}_2\text{O}_5^-) - \ln I(\text{V}_3\text{O}_8^-) \} - 0.175$$

$$\ln K^{\circ}(2) = 26^{-1/2} \{ 3 \ln I(\text{V}_2\text{O}_5^-) + 2 \ln I(\text{V}_4\text{O}_{10}^-) - 2 \ln I(\text{VO}_3^-) - 3 \ln I(\text{V}_3\text{O}_8^-) \} + 0.255$$

$$\ln K^{\circ}(3) = 30^{-1/2} \{ 2 \ln I(\text{CrO}_3^-) + 2 \ln I(\text{V}_2\text{O}_5^-) + 2 \ln I(\text{V}_4\text{O}_{10}^-) - 3 \ln I(\text{VO}_3^-) - 3 \ln I(\text{V}_3\text{O}_8^-) \} + 0.195$$

$$\ln K^{\circ}(4) = 4380^{-1/2} \{ 46 \ln I(\text{CrO}_3^-) + 21 \ln I(\text{V}_3\text{O}_8^-) + \ln I(\text{V}_4\text{O}_{10}^-) - 30 \ln I(\text{CrO}_4^-) - 9 \ln I(\text{VO}_3^-) - 29 \ln I(\text{V}_2\text{O}_5^-) \} + 0.062$$

$$\ln K^{\circ}(5) = 57378^{-1/2} \{79 \ln I(\text{CrO}_4^-) + 146 \ln I(\text{VO}_2^-) \\ + 25 \ln I(\text{V}_3\text{O}_8^-) + 29 \ln I(\text{V}_4\text{O}_{10}^-) - 53 \ln I(\text{CrO}_3^-) \\ - 115 \ln I(\text{VO}_3^-) - 111 \ln I(\text{V}_2\text{O}_5^-)\} - 0.054$$

$$\ln K^{\circ}(6) = 6^{-1/2} \{\ln I(\text{V}_2\text{O}_5^-) + \ln I(\text{CoO}_2^-) - 2(\ln \text{VO}_3^-)\} + 0.214$$

The numerical constants arrived during the transformation from ratios of partial pressures to that of ion currents (see Experimental).

Reactions (1) to (6) were chosen because the logarithms of their equilibrium constants were non-correlated with each other and possessed the same variance. Let us expatiate on this question.

Not ion currents themselves but the logarithms of equilibrium constants will be considered as primary results (the term from reference 18). This is due to the fact that the only logarithms of equilibrium constants are in thermodynamic equations that contain enthalpies of formation and entropies of substances. Applying methods of mathematical statistics to determine the enthalpies of formation and entropies will be simplified significantly if the logarithms of equilibrium constants employed are non-correlated with each other and possess the same variance.

Correlation between equilibrium constants may occur in case they are obtained from the same mass spectrum. For example, take experiments 1 to 3. Two linear independent reactions, like reactions (1) and (2), can be written down among four negative ions, currents of which were measured, and V_3O_5 , the activity of which was equal to unit in these experiments. The logarithms of the equilibrium constants look like linear transformations of the logarithms of ion currents (see above).

The logarithms of ion currents can be viewed as independent random quantities, and moreover, the hypothesis that the variance D of all the logarithms of ion currents is the same can be accepted

$$D(\ln I_{ij}) = \sigma^2$$

An amplifier measures ion currents with the same relative accuracy, and as a result, the logarithms of ion currents should have the same absolute accuracy. Considering all that, the variance of equilibrium constants is given as follows

$$D\{\ln K^0(i)\} = \sigma^2 \sum_C \nu_{iC}^2$$

and covariance (cov) between two equilibrium constants determined from the same mass spectrum can be calculated by the next formula

$$\text{cov} \{\ln K^0(i), \ln K^0(j)\} = \sigma^2 \sum_C \nu_{iC} \nu_{jC}$$

where σ^2 is the variance of the logarithm of ion current, ν_{iC} is a stoichiometric numbers (greater than zero for products and less than zero for reagents), C is a set of all ions.

As we mentioned above, we have freedom in choosing chemical reactions, i.e. in sets of stoichiometric numbers. We selected such reactions that

$$\sum_C \nu_{iC}^2 = 1 \tag{7}$$

$$\sum_C \nu_{iC} \nu_{jC} = 0 \tag{8}$$

This means that for the chosen reactions the variances of the logarithms of equilibrium constants are equal to that of the logarithm of an ion current and the logarithms of equilibrium constants are non-correlated with each other.

Eqn (7) is valid for all six reactions. Eqn (8) is kept for reactions whose equilibrium constants were computed from the same set of ion currents. Such are reactions (1) and (2), equilibrium constants of which were derived in experiments 1 to

3, and four linear independent reactions (1), (3), (4), and (5), which could be composed in experiments 4 and 5.

While estimated from different sets of ion currents, equilibrium constants are non-correlated by a definition, and Eqn (8) may not be applied. In our case this concerns reaction (6).

The estimated values of equilibrium constants of reactions (1) to (6) are given in Tables 2 to 4.

Note that according to linear algebra a set of reactions complying with Eqns (7) and (8) can always be selected.

4. Determining enthalpies of formation from equilibrium constants

Thus we obtained the set of equilibrium constants of six reactions, and from there our task was to determine the enthalpies of formation of negative ions VO_2^- , VO_3^- , V_2O_5^- , V_3O_8^- and $\text{V}_4\text{O}_{10}^-$.

4.1. Theory

The experimentally determined equilibrium constants $\ln K_{ij}$ (i enumerates the reactions, j does the equilibrium constants of the i -th reaction) are differ from the true values $\ln K_{ij}^{\text{calc}}$ on reproducibility errors ϵ_{ij}

$$\ln K_{ij} = \ln K_{ij}^{\text{calc}} + \epsilon_{ij} \quad (9)$$

The true values $\ln K_{ij}^{\text{calc}}$, in turn, are related with the enthalpies of formation and the entropies of substances included in the reactions

$$\ln K_{ij}^{\text{calc}} = R^{-1}(-T_{ij}^{-1} \cdot \vec{v}_i' \vec{H} + \vec{v}_i' \vec{S}) \quad (10)$$

were \vec{H} is the vector of enthalpies of formation, \vec{S} is the vector of entropies, \vec{v}_i' is the vector of stoichiometric numbers

of the i -th reaction. While using Eqn (10) for a small temperature interval, the enthalpies of formation and the entropies can be assumed not to depend on temperature and relate to some mean temperature.

The particular choice of reactions (1)-(6) described above brought about that the errors ε_{ij} were independent and possessed the same variance. As a result, to obtain the enthalpies of formation and the entropies the next sum of squared deviations should be minimized

$$SS = \sum_{ij} (\ln K_{ij} - \ln K_{ij}^{\text{calc}})^2 \quad (11)$$

As shown in Annex 1, the minimum of (11) upon the enthalpies of formation and the entropies is reached simultaneously with the minimum of the following sum of squares

$$SS_1 = \sum_i (b_i + R^{-1} \cdot \vec{v}_i' \vec{H})^2 P_i + \sum_i \{a_i - R^{-1} (-T_i^{-1} \cdot \vec{v}_i' \vec{H} + \vec{v}_i' \vec{S})\}^2 N_i \quad (12)$$

This allows an independent treatment of the equilibrium constants for every reaction and reduces the dimensionality of the problem considerably.

a_i and b_i in Eqn (12) are the coefficients of a straight line

$$\ln K_{ij} = b_i (T_{ij}^{-1} - T_i^{-1}) + a_i \quad (13)$$

fitting the logarithms of the equilibrium constants from inverse temperature, where

$$T_i^{-1} = (\sum_j T_{ij}^{-1}) / N_i \quad (14)$$

is the mean temperature. According to the least squares method these coefficients are estimated as follows

$$a_i = (\sum_j \ln K_{ij}) / N_i \quad (15)$$

$$b_i = \{ \sum_j \ln K_{ij} (T_{ij}^{-1} - T_i^{-1}) \} / P_i \quad (16)$$

where N_i is the number of the equilibrium constants in the i -th reaction, and

$$P_i = \sum_j (T_{ij}^{-1} - T_i^{-1})^2 \quad (17)$$

Finding the minimum of squared deviations (12) corresponds to solving a system of linear equations

$$\begin{pmatrix} \vec{B} \\ \vec{a} \end{pmatrix} = R^{-1} \begin{pmatrix} -\mathbb{X} & \mathbb{O} \\ -\mathbb{T}^{-1}\mathbb{X} & \mathbb{X} \end{pmatrix} \begin{pmatrix} \vec{H} \\ \vec{S} \end{pmatrix} \quad (18)$$

with the consistent weights (see Annex 2). In Eqn (18) \vec{a} and \vec{B} are the vectors of coefficients a_i and b_i correspondingly; \mathbb{X} is the stoichiometric matrix, the i -th row of which is the transposed stoichiometric vector of the i -th reaction, $\mathbb{X} = (\vec{v}_1, \dots, \vec{v}_R)'$; $\mathbb{T} = \text{diag}\{T_i\}$; \mathbb{O} is the zero matrix.

Naturally, all the enthalpies of formation and the entropies in Eqn (18) can not be estimated. The matrix \mathbb{X} always have an incomplete rang according to the mass conservation law. To find a solution, all the substances must be divided to the sets formed from substances with the known (Ah) and unknown (Bh) enthalpies of formation, with the known (As) and unknown (Bs) entropies. In common case these separations of the substances by enthalpies of formation and by entropies can differ from each other. The only necessary condition is that the parts of the stoichiometric matrix \mathbb{X} corresponding to the substances with enthalpies and entropies to be found, the matrices \mathbb{X}_{Bh} and \mathbb{X}_{Bs} correspondingly, must have a full rang.

Two extreme cases of separating the substances to the sets As and Bs match processing by the Second and Third Laws. The Second Law treatment coincides with the case in which the matrix \mathbb{X}_{Bs} has a maximum available rang (the rang of the matrix \mathbb{X}), the Third Law treatment does with the empty set Bs, when the entropies of all the substances are assumed to be known.

Finding the minimum of the sum of squared deviations (12) is described in Annex 2 and computing the errors of the

enthalpies of formation and the entropies to be found is in Annex 3.

4.2. Calculations

As described in part 2 (Experimental), several mass spectra, and consequently several equilibrium constants, were measured at the same temperature in an experiment. The mean of the logarithms of such equilibrium constants ($\ln K_{im}$), the standard deviation of single values of equilibrium constants (s_{im}), and the number of values at (n_{im}) the temperature T_{im} are presented in Table 2-4. Note that in Eqns (11), (14) to (17), and (27), the summation over the index j includes not the average values $\ln K_{im}$ but the single values $\ln K_{ij}$. To use the average values, these equations must slightly be modified. For example, Eqns (15) and (16) should look like as follows

$$a_i = (\sum_m \ln K_{im} \cdot n_{im}) / N_i$$

$$b_i = \{ \sum_m \ln K_{im} (T_{im}^{-1} - T_i^{-1}) n_{im} \} / P_i$$

Table 5 summarizes processing the equilibrium constants of reactions (1) to (6) according to Eqns (14) to (17). Two standard deviations for each reaction were possible to estimate, namely, the pooled standard deviation $s_{p,i}$

$$s_{p,i}^2 = \sum_m s_{im}^2 (n_{im} - 1) / (N_i - M_i) \quad (19)$$

and the standard deviation of the fit $s_{f,i}$

$$s_{f,i}^2 = \sum_m (\ln K_{im} - b_i (T_{im}^{-1} - T_i^{-1}) + a_i)^2 n_{im} / (M_i - 2) \quad (20)$$

Here the summation is only over different temperatures T_{im} , and M_i is the number of the different temperatures in the i -th reaction.

Both variances $s_{p,i}^2$ and $s_{f,i}^2$ are the estimates of the variance of the equilibrium constants σ^2 while their origin is different. $s_{p,i}$ is due to replicate measurements and $s_{f,i}$ is

due to deviation of the average values from the fitting equation. In Table 5 they are close to each other except for reaction (5), where the standard deviation of the fit is much greater than the pooled standard deviation. We made following explanation. The measured ion current of VO_2^- , included in the only reaction (5), was close to the background. This raised its imprecision and make its temperature behavior somewhat "wrong". To correct that in the following treatment, weights of the reaction (5) (values of N_5 and P_5) were lowered by the factor four.

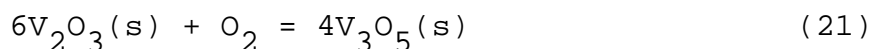
In our case, the set Bh comprises six substances with enthalpies of formation to be found: VO_2^- , VO_3^- , V_2O_5^- , V_3O_8^- , $\text{V}_4\text{O}_{10}^-$, and CoO_2^- . The set Ah includes the other five compounds in reactions (1) to (6), which the enthalpies of formation are known: $\text{Cr}_2\text{O}_3(\text{s})$, $\text{CoO}(\text{s})$, $\text{V}_3\text{O}_5(\text{s})$, CrO_3^- , and CrO_4^- .

Seeing that the investigated temperature interval was small and the reproducibility error was comparatively large (20-30% in the equilibrium constants, see $s_{f,i}$ and $s_{p,i}$ in Table 5), the entropies of all six substances in the set Bh were impossible to determine reliably. The inaccuracy of the entropies of VO_2^- , VO_3^- , $\text{V}_4\text{O}_{10}^-$, and CoO_2^- was much less while the entropies were derived from the molecular constants being estimated. Therefore, we put in the set Bs only two negative ions V_2O_5^- and V_3O_8^- , for which we have not found any analogous neutral molecules good enough to estimate the molecular constants. The other nine compounds formed the set As with the entropies assumed to be known a priori.

Table 6 lists the enthalpies of formation and the entropies chosen for the substances in the sets Ah and As. The entropies of ions VO_2^- and $\text{V}_4\text{O}_{10}^-$ were received based on the data

on neutral molecules VO_2 and V_4O_{10} from the reference book (19). Ions were assumed to have the same molecular constants except the orbital degeneracy: $g_o = 1$ for VO_2^- and $g_o = 2$ for $\text{V}_4\text{O}_{10}^-$.

The thermodynamics of the oxide V_3O_5 was obtained from the reaction



To this end, the data of Vasil'eva et al's (24) (at 1400 K $\Delta_r H_m^\circ = -428.6 + 5.9 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_r S_m^\circ = -136.1 + 4.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and data for V_2O_3 and oxygen from reference book (19) were used. The thermodynamics of reaction (21) was also investigated by other authors, (25-30) the discussion being held in references 24 and 31 and in reviews. (32-34) As a whole, the data of these works for reaction (21) are in a good agreement. Our choice was made up because in reference 24 the experimental data were recalculated to stoichiometric V_2O_3 and made in the temperature interval close to ours.

As already mentioned, the enthalpies of formation and entropies at mean temperature should stay in Eqns (10), (12) and (18). To ease the application of the reference books, the mean temperature was rounded, and thus, the value 1400 K was used as the mean temperature.

Applying the enthalpy of formation at 1400 K, i.e. computing the difference $\{\Delta_f H_m^\circ(1400 \text{ K}) - \Delta_f H_m^\circ(0 \text{ K})\}$, it is not that easy. The reference state of elements is changing while temperature is altering and this makes breakdowns in the value of the enthalpy of formation. Utilization of the practical enthalpy often used in technique, i.e. the quantity $\{\Delta_f H_m^\circ(0 \text{ K}) + \Delta_0^{1400} H_m^\circ\}$. is a lot less complicated. Here the enthalpy of formation at 0 K and the difference $\Delta_0^{1400} H_m^\circ$, which is facile to

calculate, are only needed. So we took the second way in our work, although both of them bring to same results.

Table 7 present the enthalpies of formation and the entropies obtained by Eqn (33). To estimate inaccuracy of the values, squares of the full uncertainties instead variances and the quadrupled minimal value of (12) instead of σ^2 were substituted in Eqns (35) and (36). The errors of the values used a priori and given in Table 6 were used as the diagonal members of the dispersion matrices $\mathbb{D}(\vec{H}_{Ah})$ and $\mathbb{D}(\vec{S}_{As})$. The three non-zero members of the matrix $\text{COV}(\vec{H}_{Ah}, \vec{S}_{As})$ $\{\text{cov}[H^\circ(\text{CrO}_3^-), S^\circ(\text{CrO}_3^-)] = 21 \text{ kJ}\cdot\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-2}$, $\text{cov}[H^\circ(\text{CrO}_4^-), S^\circ(\text{CrO}_4^-)] = 44 \text{ kJ}\cdot\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-2}$, $\text{cov}[H^\circ(\text{V}_3\text{O}_5), S^\circ(\text{V}_3\text{O}_5)] = 1.7 \text{ kJ}\cdot\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-2}\}$ and the only non-zero non-diagonal member of the matrix $\mathbb{D}(\vec{H}_{Ah})$ $\{\text{cov}[H^\circ(\text{CrO}_3^-), H^\circ(\text{CrO}_4^-)] = 57 \text{ kJ}^2\cdot\text{mol}^{-2}\}$ were also added. The last values were obtained by us during the combined treatment in Ref. [10] (unfortunately they are not listed there) and while processing the equilibrium constants of reaction (21) from reference (24).

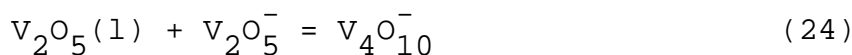
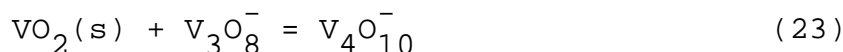
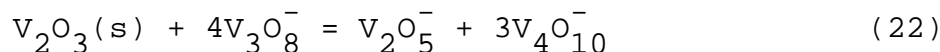
The covariations among the obtained values (non-diagonal members in Eqn 35) and among the obtained and auxiliary values (Eqn 36) are recorded in Table 8.

5. Determining the activities of vanadium oxides and the oxygen partial pressure

Now, after obtaining the thermodynamics of negative ions VO_2^- , VO_3^- , V_2O_5^- , V_3O_8^- , and $\text{V}_4\text{O}_{10}^-$, the methods can be devised to employ them for conventional tasks of high temperature mass spectrometry as determining activities of condensed phases and partial pressures of neutral molecules.

Let us begin with the activities of vanadium oxides. They

are needed, for example, to analyze processes of preparing steel. (35-37) The nature of what we suggest is the same as in heterogeneous equilibria method, but the ratios of partial pressures of vanadium-containing negative ions will be applied as measurable quantities (see also (1,12)). The reaction, analogous to (2), can be written down for each vanadium oxide. For example



The enthalpies and entropies of these reactions at 1400 K can be calculated from the data of Tables 6 and 7. This gives the expressions to equilibrium constants of reactions (22)-(24) as follows

$$\ln K^O(22) = 2490/T - 0.78$$

$$\ln K^O(23) = 5890/T - 2.77$$

$$\ln K^O(24) = 36680/T - 15.32$$

As a result, measuring ion currents $V_2O_5^-$, $V_3O_8^-$, and $V_4O_{10}^-$ in the vapors of the mixture under study one can estimate the activities of vanadium oxides

$$a(V_2O_3) = \frac{p(V_2O_5^-)p(V_4O_{10}^-)^3}{p(V_3O_8^-)^4} \frac{1}{K^O(22)}$$

$$a(VO_2) = \frac{p(V_4O_{10}^-)}{p(V_3O_8^-)} \frac{1}{K^O(23)}$$

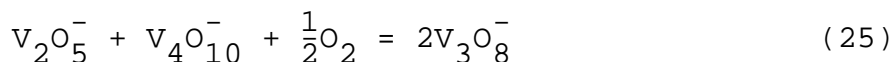
$$a(V_2O_5) = \frac{p(V_4O_{10}^-)}{p(V_2O_5^-)} \frac{1}{K^O(24)}$$

Arrival of such negative ions should be expected at temperatures above 1200 K because of their high stability. However, if the electron concentration in the system under study were not high enough to generate these ions it could

always be enhanced by using an easy-ionized admixture (see examples with other ions elsewhere (12)).

Table 9 shows the activities of vanadium oxides estimated for experiments 4 and 5, where composition of vanadium oxide was about 2 moles per cent.

The same approach can be employed to determine the oxygen partial pressure. One of possible reactions to that is



Again the data of Tables 6 and 7 allows estimating the equilibrium constants

$$\ln K^O(25) = 33110/T - 12.88$$

and the formula for the oxygen pressure looks as follows

$$p(O_2)/p^O = \frac{p(V_3O_8^-)^2}{p(V_2O_5^-)p(V_4O_{10}^-)} \frac{1}{K^O(25)}$$

Figure 1 displays the oxygen partial pressures estimated by the proposed method in experiments 1 to 3. The experimental pressures is compared with the literature data on oxygen pressure for heterogeneous equilibria V_2O_3/V_3O_5 and V_3O_5/V_4O_7 . As one could expected, the measured pressures lies inside the stability region of V_3O_5 within experimental uncertainties.

In conclusion of this part, we will stop by estimating the accuracy of the equilibrium constants of reactions (22)-(25). Since the errors of the enthalpies of formation and the entropies presented in Tables 6 and 7 are correlated between each other (see Table 8) the error propagation law must be applied in its general form (for example, see discussion in reference 11)

$$R^2 D\{\ln K^O\} = \frac{1}{T^2} \{ \vec{v}' D(\vec{H}) \vec{v} \} + \vec{v}' D(\vec{S}) \vec{v} - \frac{1}{T} \{ \vec{v}' \text{COV}(\vec{H}, \vec{S}) \vec{v} + \vec{v}' \text{COV}(\vec{S}, \vec{H}) \vec{v} \}$$

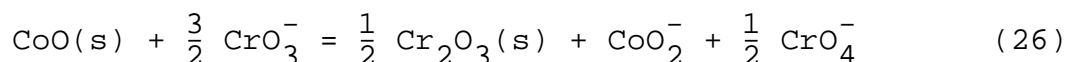
Here are included the covariations {the matrix $\text{COV}(\vec{H}, \vec{S})$ and non-diagonal members of $\mathbb{D}(\vec{H})$ and $\mathbb{D}(\vec{S})$ } besides the errors of the enthalpies of formation and the entropies.

We will give a small numerical example for the equilibrium constant of reaction (25) at 1400 K. Were the covariations not used the greatly enhanced inaccuracy would be obtained: ± 12 in $\ln K^\circ$, which corresponds to the error in $K^\circ(25)$ on about five orders of magnitude. Only application of the covariations from Table 8 supplies the reliable inaccuracy which is just ± 0.56 in $\ln K^\circ$ or 75% in K° itself.

6. Electron affinity and dissociation energies

Negative ions VO_2^- , VO_3^- , V_2O_5^- , V_3O_8^- , and $\text{V}_4\text{O}_{10}^-$, observed by us in the gas phase are not common for solution and solid chemistry of vanadium where multi-charged polymeric ions like VO_4^{3-} and V_3O_9^- exist. The same situation is with sulfates. The double-charged negative ion SO_4^{2-} is mainly seen in the condensed phase, but only single-charged negative ions SO_3^- , SO_4^- , and MSO_4^- are presented in the gas phase ⁽³⁸⁾ because of instability of isolated sulfate-anion.

As mentioned above, the reliability of determined thermodynamic parameters mainly depends on establishing equilibrium in the effusion cell. The following facts witness that equilibrium has been achieved. The enthalpy of formation of CoO_2^- as determined in our work ($-152 \pm 13 \text{ kJ} \cdot \text{mol}^{-1}$) is close to that in reference 2 ($-148 \pm 11 \text{ kJ} \cdot \text{mol}^{-1}$) where the equilibrium constants of the reaction



were measured. The equilibrium constants of reactions (3), (4),

and (5) (see Table 3) were estimated in two experiments 4 and 5, and they were in good agreement with each other while the activity of vanadium oxide differed in almost ten times. The equilibrium constants of reaction (1) determined in experiments 1 to 5 also agreed with each other.

Using the enthalpies of formation determined by us (Table 7) and the literature data $\{\Delta_f H_0^{\circ}(O^-) = (105.6 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_0^{\circ}(\text{VO}) = (148.8 \pm 10) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_0^{\circ}(\text{VO}_2) = (-230 \pm 15) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_0^{\circ}(\text{V}_4\text{O}_{10}) = (-2800 \pm 40) \text{ kJ} \cdot \text{mol}^{-1}$ (19) $\}$, the electron affinity and dissociation energies have been estimated $\text{EA}(\text{VO}_2) = (223 \pm 20) \text{ kJ} \cdot \text{mol}^{-1}$, $\text{EA}(\text{V}_4\text{O}_{10}) = (401 \pm 61) \text{ kJ} \cdot \text{mol}^{-1}$, $D(\text{VO}-\text{O}^-) = (708 \pm 17) \text{ kJ} \cdot \text{mol}^{-1}$, $D(\text{VO}_2-\text{O}^-) = (630 \pm 19) \text{ kJ} \cdot \text{mol}^{-1}$.

One may compare the obtained electron affinity with that of phosphorus oxides $\text{EA}(\text{PO}_2) = (367 \pm 21) \text{ kJ} \cdot \text{mol}^{-1}$ and $\text{EA}(\text{P}_4\text{O}_{10}) = (313 \pm 23) \text{ kJ} \cdot \text{mol}^{-1}$. (39) The reverse tendency is seen, the electron affinity of PO_2 is greater than one of P_4O_{10} while it rises with transition from VO_2 to V_4O_{10} (see discussion in reference (39)).

Annex 1. Transforming the sum of squared deviations

Let us rewrite the sum of squares (11) adding and subtracting the right part of Eqn (13)

$$\text{SS} = \sum_{ij} \{ [\ln K_{ij} - b_i(T_{ij}^{-1} - T_i^{-1}) + a_i] + [b_i(T_{ij}^{-1} - T_i^{-1}) + a_i - \ln K_{ij}^{\text{calc}}] \}^2$$

Now open the braces up. As a result, we will obtain

$$\text{SS} = \sum_{ij} [\ln K_{ij} - b_i(T_{ij}^{-1} - T_i^{-1}) + a_i]^2 + \sum_{ij} [b_i(T_{ij}^{-1} - T_i^{-1}) + a_i - \ln K_{ij}^{\text{calc}}]^2 \quad (27)$$

The cross product vanishes because of the relations (14)-(17).

The first sum of squares in Eqn (27) exhibits scatter of the experimental equilibrium constants over the straight lines

(13), which were obtained during independent treatment of each reaction, and does not depend on the parameters to be found - the enthalpies of formation and the entropies. It means that the minimum of (11) versus unknown enthalpies of formation and entropies is reached simultaneously with the minimum of the second sum of squares in (27) (denote it as SS_1). It characterizes the deviation of the final fitting equations over the straight lines (13).

Substituting the expression for $\ln K_{ij}^{calc}$ (Eqn 10) inside SS_1 in turn and rearranging it we obtain

$$SS_1 = \sum_{ij} \{ (b_i + R^{-1} \cdot \vec{v}_i' \vec{H}) (T_{ij}^{-1} - T_i^{-1}) + [a_i - R^{-1} (-T_i^{-1} \cdot \vec{v}_i' \vec{H} + \vec{v}_i' \vec{S})] \}^2$$

While the braces are opened and the summation by the index j is done, the required formula (12) for the sum of squares will appear. The cross product will be equal to zero because of Eqn (14).

Annex 2. Determining unknown enthalpies of formation and entropies

While the vector \vec{H}_{Ah} of the enthalpies of formation and the vector \vec{S}_{As} of the entropies are taken a priori, the minimum of squared deviations (12) can be found by solving the system of linear equations with corresponded weights as follows (compare with Eqn 18)

$$\vec{Y} = R^{-1} \begin{pmatrix} -X_{Bh} & 0 \\ -T^{-1} X_{Bh} & X_{Bs} \end{pmatrix} \begin{pmatrix} \vec{H}_{Bh} \\ \vec{S}_{Bs} \end{pmatrix} \quad (28)$$

where

$$\vec{Y} = \begin{pmatrix} \vec{b} \\ \vec{a} \end{pmatrix} - R^{-1} \begin{pmatrix} -X_{Ah} & 0 \\ -T^{-1} X_{Ah} & X_{As} \end{pmatrix} \begin{pmatrix} \vec{H}_{Ah} \\ \vec{S}_{As} \end{pmatrix} \quad (29)$$

and indices As, Ah, Bs, and Bh show that quantities relate to such sets.

The values of the vectors \vec{H}_{Ah} and \vec{S}_{As} are taken from the literature data (see Table 6) and are known with some inaccuracy, however, we don't want them to be changed even in a small extent during the minimization. It means that they must not be considered as additional equations and their inaccuracies should be disregarded for this moment (see discussion in reference 11). Hence, the weight matrix to solve the system (28) should only be based on the dispersion matrix of the vectors \vec{a} and \vec{b} . One may understand this point better by going from Eqn (12) to Eqn (28) on his own.

The coefficients a_i and b_i , forming the vectors \vec{a} and \vec{b} , are computed according to Eqns (15) and (16). The analysis of these equations gives that the vectors \vec{a} and \vec{b} are non-correlated and their dispersion matrices are diagonal

$$\mathbb{D}(\vec{a}) = \sigma^2 \text{diag}\{N_i^{-1}\} \quad (30)$$

$$\mathbb{D}(\vec{b}) = \sigma^2 \text{diag}\{P_i^{-1}\} \quad (31)$$

where σ^2 is the variance of logarithm of experimental equilibrium constants, which was assumed to be the same for all the reactions because of the special choice of stoichiometric numbers. As a result, the weight matrix to solve the system (28) should look as follows

$$W = \begin{pmatrix} P & \mathbb{O} \\ \mathbb{O} & N \end{pmatrix} \quad (32)$$

where N and P are the diagonal matrices consisting from the values of N_i and P_i correspondingly, and \mathbb{O} is the zero matrix.

The theory of least squares method ⁽⁴⁰⁾ supplies the solution to the system of linear equations (28) with the weight matrix (32), which at the same time minimizes (12), as follows

$$\begin{pmatrix} \vec{H}_{Bh} \\ \vec{S}_{Bs} \end{pmatrix} = R \cdot A \vec{Y} \quad (33)$$

where

$$A = \left\{ \left[\begin{pmatrix} -X_{Bh} & 0 \\ -T^{-1}X_{Bh} & X_{Bs} \end{pmatrix}' \begin{pmatrix} P & 0 \\ 0 & N \end{pmatrix} \begin{pmatrix} -X_{Bh} & 0 \\ -T^{-1}X_{Bh} & X_{Bs} \end{pmatrix} \right]^{-1} \begin{pmatrix} -X_{Bh} & 0 \\ -T^{-1}X_{Bh} & X_{Bs} \end{pmatrix}' \begin{pmatrix} P & 0 \\ 0 & N \end{pmatrix} \right\} \quad (34)$$

Annex 3. Estimating inaccuracies of the parameters to be found

Having obtained the solution (33) which brings the sum of squares (12) to the minimum, we have to remember about uncertainties of the auxiliary values and to include them into the inaccuracy of the solution.

According to Eqn (33) the enthalpies of formation and the entropies to be found look like the linear transformation of the vector \vec{Y} which in turn is the sum of linear transformations of two compound vectors (Eqn 29).

The dispersion matrix of the first vector composed from the coefficients a_i and b_i is given by Eqns (30) and (31). Naturally, this vector is not correlated not with \vec{H}_{Ah} , neither with \vec{S}_{As} . We compute it from the experimental equilibrium constants, the variances of which are not tied by any means with the variances of the auxiliary data. The dispersion matrix of the second compound vector in Eqn (29) should be taken from the literature data besides the values themselves. Note that in the common case the vectors \vec{H}_{Ah} and \vec{S}_{As} are correlated with each other what is described by the covariance matrix

$$\text{COV}(\vec{H}_{Ah}, \vec{S}_{As}) = \text{COV}(\vec{S}_{As}, \vec{H}_{Ah})'$$

This matrix is equal to zero in case these vectors are non-correlated.

The dispersion matrix of the parameters to be found can be estimated according to mathematical statistics ⁽⁴⁰⁾ as follows

$$D \begin{pmatrix} \vec{H}_{Bh} \\ \vec{S}_{Bs} \end{pmatrix} = \begin{pmatrix} D(\vec{H}_{Bh}) & \text{COV}(\vec{H}_{Bh}, \vec{S}_{Bs}) \\ \text{COV}(\vec{S}_{Bs}, \vec{H}_{Bh}) & D(\vec{S}_{Bs}) \end{pmatrix} =$$

$$A \left\{ R^2 \sigma^2 \begin{pmatrix} P^{-1} & 0 \\ 0 & N^{-1} \end{pmatrix} + \begin{pmatrix} -X_{Ah} & 0 \\ -T^{-1}X_{Ah} & X_{As} \end{pmatrix} D \begin{pmatrix} \vec{H}_{Ah} \\ \vec{S}_{As} \end{pmatrix} \begin{pmatrix} -X_{Ah} & 0 \\ -T^{-1}X_{Ah} & X_{As} \end{pmatrix}' \right\} A' \quad (35)$$

where the matrix

$$D \begin{pmatrix} \vec{H}_{Ah} \\ \vec{S}_{As} \end{pmatrix} = \begin{pmatrix} D(\vec{H}_{Ah}) & \text{COV}(\vec{H}_{Ah}, \vec{S}_{As}) \\ \text{COV}(\vec{S}_{As}, \vec{H}_{Ah}) & D(\vec{S}_{As}) \end{pmatrix}$$

is taken from literature.

The parameters to be found are correlated with the auxiliary values. The covariance matrix describing that can be estimated by the following equation

$$\text{COV} \left\{ \begin{pmatrix} \vec{H}_{Bh} \\ \vec{S}_{Bs} \end{pmatrix}, \begin{pmatrix} \vec{H}_{Ah} \\ \vec{S}_{As} \end{pmatrix} \right\} = -A \begin{pmatrix} -X_{Ah} & 0 \\ -T^{-1}X_{Ah} & X_{As} \end{pmatrix} D \begin{pmatrix} \vec{H}_{Ah} \\ \vec{S}_{As} \end{pmatrix} \quad (36)$$

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TABLE 1. The mixtures under study (composition, moles per cent) and observed mass spectra of negative ions (relative units, 1387 K, data for the isotope ^{51}Cr are given for chromium-containing ions)

1	$\text{V}_3\text{O}_5 + \text{K}_2\text{CrO}_4$ (96:4)	VO_3^- (6.3), V_2O_5^- (7.6), V_3O_8^- (260), $\text{V}_4\text{O}_{10}^-$ (1000)
2	V_3O_5	VO_3^- (7.1), V_2O_5^- (6.7), V_3O_8^- (290), $\text{V}_4\text{O}_{10}^-$ (1000)
3	V_3O_5	VO_3^- (54), V_2O_5^- (45), V_3O_8^- (370), $\text{V}_4\text{O}_{10}^-$ (1000)
4	$\text{Cr}_2\text{O}_3 + \text{V}_3\text{O}_5 + \text{K}_2\text{CrO}_4$ (96:2:2)	VO_2^- (1.8), VO_3^- (17 000), V_2O_5^- (930), V_3O_8^- (6 200), $\text{V}_4\text{O}_{10}^-$ (980), CrO_3^- (100 000), CrO_4^- (28)
5	$\text{Cr}_2\text{O}_3 + \text{V}_3\text{O}_5 + \text{K}_2\text{CrO}_4$ (98:1:1)	VO_2^- (2.5), VO_3^- (5400), V_2O_5^- (130), V_3O_8^- (340), $\text{V}_4\text{O}_{10}^-$ (22), CrO_3^- (100 000), CrO_4^- (28)
6	$\text{CoO} + \text{Cr}_2\text{O}_3 + \text{K}_2\text{CrO}_4 +$ $+\text{V}_3\text{O}_5$ (94:3:2:1) ^a	CoO_2^- (0.33), VO_3^- (1000), V_2O_5^- (75)

^a at 1430 K

TABLE 2. Standard equilibrium constants of reactions (1) and (2); s_m is the calculated deviation of single values; n_m is the number of measurements

Expt no.	T K	$\ln\{K^{\circ}(1)\}$	s_m	n_m	$\ln\{K^{\circ}(2)\}$	s_m	n_m
1	1209.	0.71	0.06	4	-0.17	0.06	4
	1255.	0.62	0.09	6	-0.12	0.06	6
	1300.	0.59	0.04	7	-0.06	0.06	7
	1344.	0.44	0.10	3	-0.03	0.09	3
	1387.	0.40	0.11	3	0.16	0.03	3
2	1255.	0.60	0.11	6	-0.16	0.13	6
	1300.	0.51	0.05	8	-0.12	0.10	8
	1344.	0.50	0.14	9	-0.02	0.15	9
	1387.	0.46	0.18	10	-0.02	0.12	10
	1430.	0.32	0.19	9	0.11	0.08	9
	1473.	0.10	0.14	10	0.08	0.14	10
	1515.	0.20	0.23	6	0.08	0.08	6
3	1300.	0.46	0.02	2	-0.07	0.02	2
	1344.	0.40	0.17	6	0.07	0.13	6
	1387.	0.41	0.16	4	0.17	0.08	4
	1430.	0.20	0.10	3	0.16	0.07	3
	1473.	0.24	0.09	4	0.19	0.08	4
4	1255.	0.96	0.09	4			
	1300.	0.85	0.05	7			
	1344.	0.63	0.05	5			
	1387.	0.58	0.02	3			
	1430.	0.45	0.09	3			
5	1300.	0.86	0.14	3			
	1344.	0.64	0.16	3			
	1387.	0.52	0.09	6			
	1430.	0.47	0.18	3			
	1455.	0.40	0.00	1			

TABLE 3. Standard equilibrium constants of reactions (3) to (5); s_m is the calculated deviation of single values; n_m is the number of measurements

Expt no.	T K	$\ln\{K^O(3)\}$	s_m	n_m	$\ln\{K^O(4)\}$	s_m	n_m	$\ln\{K^O(5)\}$	s_m	n_m
4	1255.	-0.79	0.02	4						
	1300.	-0.83	0.05	7	5.41	0.10	5			
	1344.	-0.75	0.03	5	5.18	0.04	5	-6.39	0.00	1
	1387.	-0.73	0.01	3	5.10	0.04	3	-7.26	0.09	3
	1430.	-0.60	0.04	3	4.93	0.22	3	-7.08	0.23	3
5	1300.	-0.97	0.13	3	5.31	0.11	3			
	1344.	-0.85	0.02	3	5.28	0.04	3			
	1387.	-0.59	0.03	6	5.14	0.14	6	-6.35	0.15	6
	1430.	-0.68	0.17	3	4.99	0.11	3	-6.81	0.23	3
	1455.	-0.83	0.00	1	4.90	0.00	1	-6.29	0.00	1

TABLE 4. Standard equilibrium constants of reaction (6); s_m is the calculated deviation of single values; n_m is the number of measurements

Expt no.	\underline{T} K	$\ln K^{\circ}(6)$	s_m	n_m
6	1370.	-4.26	0.04	2
	1430.	-4.12	0.06	9
	1515.	-4.13	0.15	12

TABLE 5. Results of processing the equilibrium constants (see Eqns 14 to 17, 19 and 20)

Reaction no.	T K	$\frac{b_i}{\text{kK}}$	a_i	N_i	$\frac{P_i^{1/2}}{\text{kK}^{-1}}$	s_p	s_f
(1)	1358.	4.02	0.49	138	0.486	0.13	0.28
(2)	1361.	-2.06	0.00	100	0.444	0.11	0.15
(3)	1347.	-2.35	-0.75	38	0.193	0.07	0.18
(4)	1363.	5.65	5.17	32	0.147	0.11	0.09
(5)	1403.	6.76	-6.72	17	0.058	0.18	0.75
(6)	1467.	-0.84	-4.13	23	0.114	0.12	0.16

TABLE 6. The auxiliary enthalpies of formation and entropies^a; $H_m^O(1400\text{ K})$ stands for the quantity $\{\Delta_f H_m^O(0\text{ K}) + \Delta_0^{1400} H_m^O\}$; standard pressure is 101325 Pa

substance	$\frac{\Delta_f H_m^O(0\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_0^{1400} H_m^O}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{H_m^O(1400\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{S_m^O(1400\text{ K})}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
$\text{Cr}_2\text{O}_3(\text{s})$	-1134.8±1.7	152.1	-982.7	268.9±1.3
$\text{V}_2\text{O}_3(\text{s})$	-1211.7±5.0	159.5	-1052.2	288.8±3.6
$\text{V}_3\text{O}_5(\text{s})^{\text{b}}$			-1674.1±7.6	463.0±5.5
$\text{VO}_2(\text{s})$	-711.4±2.5	97.7	-613.7	174.5±1.8
$\text{V}_2\text{O}_5(\text{s},1)^{\text{c}}$	-1547.3±5.5	274.8	-1272.9	450.9±4.6
$\text{CoO}(\text{s})^{\text{d}}$	-237.8±1.3	70.7	-167.1	137.8±1.7
O_2	0	45.6	45.6	255.5±0.0
$\text{CrO}_3^-^{\text{e}}$	-669±9	97.5	-571.5	391.7±4.0
$\text{CrO}_4^-^{\text{e}}$	-781±11	119.9	-661.1	432.2±5.8
$\text{VO}_2^-^{\text{b}}$		68.5		334.5±2.5
$\text{VO}_3^-^{\text{f}}$		95.5		380.0±5.2
$\text{V}_4\text{O}_{10}^-^{\text{b}}$		366.2		894.5±30
$\text{CoO}_2^-^{\text{g}}$		70.7		342.4±4.4

^a Unless specified otherwise, the data from the Gurvich's reference book (19) were taken

^b See text

^c From reference 20

^d From the data bank IVTAN-TERMO (1986 version) (21)

^e From reference 10

^f From references 22, 23

^g From reference 2

TABLE 7. The obtained enthalpies of formation and entropies;
 $H_m^O(1400\text{ K})$ stands for the quantity $\{\Delta_f H_m^O(0\text{ K}) + \Delta_0^{1400} H_m^O\}$; standard
pressure is 101325 Pa

ion	$\frac{H_m^O(1400\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_f H_m^O(0\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{S_m^O(1400\text{ K})}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
VO_2^-	-384.7±13.5	-453.2	
VO_3^-	-658.6±11.8	-754.1	
V_2O_5^-	-1256.8±26.5		570.9±17.5
V_3O_8^-	-2172.0±43.7		743.0±29.3
$\text{V}_4\text{O}_{10}^-$	-2834.7±46.3	-3200.9	
CoO_2^-	-81.5±12.7	-152.2	

TABLE 8. Covariances among the obtained parameters and the auxiliary data; $\text{cov}(H, H)$ in $\text{kJ}^2 \cdot \text{mol}^{-2}$, $\text{cov}(H, S)$ in $\text{J} \cdot \text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-2}$, $\text{cov}(S, S)$ in $\text{J}^2 \cdot \text{K}^{-2} \cdot \text{mol}^{-2}$

	$H(\text{V}_2\text{O}_5^-)$	$H(\text{V}_3\text{O}_8^-)$	$H(\text{VO}_2^-)$	$H(\text{VO}_3^-)$	$H(\text{V}_4\text{O}_{10}^-)$	$H(\text{CoO}_2^-)$	$S(\text{V}_2\text{O}_5^-)$	$S(\text{V}_3\text{O}_8^-)$
$H(\text{V}_2\text{O}_5^-)$	701.	514.	90.	150.	532.	111.	411.	231.
$H(\text{V}_3\text{O}_8^-)$	514.	1912.	121.	141.	1758.	91.	229.	1167.
$H(\text{VO}_2^-)$	90.	121.	183.	83.	140.	70.	-8.	4.
$H(\text{VO}_3^-)$	150.	141.	83.	138.	156.	66.	31.	3.
$H(\text{V}_4\text{O}_{10}^-)$	532.	1758.	140.	156.	2140.	96.	214.	1005.
$H(\text{CoO}_2^-)$	111.	91.	70.	66.	96.	161.	30.	14.
$S(\text{V}_2\text{O}_5^-)$	411.	229.	-8.	31.	214.	30.	305.	171.
$S(\text{V}_3\text{O}_8^-)$	231.	1167.	4.	3.	1005.	14.	171.	860.
$H(\text{Cr}_2\text{O}_3)$	37.	55.	18.	18.	74.	0.	0.	0.
$H(\text{V}_3\text{O}_5)$	-1.	-1.	-1.	-1.	-1.	-1.	0.	0.
$H(\text{CoO})$	0.	0.	0.	0.	0.	2.	0.	0.
$H(\text{CrO}_3^-)$	54.	60.	47.	52.	61.	50.	0.	0.
$H(\text{CrO}_4^-)$	56.	64.	53.	56.	64.	55.	-1.	1.
$S(\text{VO}_2^-)$	0.	0.	9.	0.	0.	0.	0.	0.
$S(\text{VO}_3^-)$	31.	5.	-2.	36.	-1.	-4.	23.	4.
$S(\text{V}_4\text{O}_{10}^-)$	219.	1004.	7.	-1.	1223.	16.	161.	738.
$S(\text{CoO}_2^-)$	0.	0.	0.	0.	0.	28.	0.	0.
$S(\text{Cr}_2\text{O}_3)$	-20.	-45.	-13.	-13.	-52.	1.	4.	-4.
$S(\text{V}_3\text{O}_5)$	1.	1.	1.	1.	1.	1.	0.	0.
$S(\text{CoO})$	0.	0.	0.	0.	0.	-4.	0.	0.
$S(\text{CrO}_3^-)$	0.	1.	-2.	-1.	1.	-1.	0.	0.
$S(\text{CrO}_4^-)$	-2.	-2.	3.	0.	-3.	1.	-1.	1.

TABLE 9. Activities of vanadium oxides in the mixture $\{\text{Cr}_2\text{O}_3+\text{V}_3\text{O}_5\}$
 $\{R_1 = I(\text{V}_2\text{O}_5^-)I(\text{V}_4\text{O}_{10}^-)^3/I(\text{V}_3\text{O}_8^-), R_2 = I(\text{V}_4\text{O}_{10}^-)/I(\text{V}_3\text{O}_8^-),$
 $R_3 = I(\text{V}_4\text{O}_{10}^-)/I(\text{V}_2\text{O}_5^-)\}$

Expt no	T K	ln R ₁	n _m	a(V ₂ O ₃)	ln R ₂	n _m	a(VO ₂)	ln R ₃	n _m	a(V ₂ O ₅)
4	1255	-7.27	4	2.9·10 ⁻⁴	-1.19	4	5.8·10 ⁻²	2.51	4	2.3·10 ⁻⁵
	1300	-7.39	7	2.8·10 ⁻⁴	-1.47	7	5.1·10 ⁻²	1.49	7	2.2·10 ⁻⁵
	1344	-7.38	5	3.0·10 ⁻⁴	-1.69	5	4.8·10 ⁻²	0.63	5	2.4·10 ⁻⁵
	1387	-7.46	3	2.9·10 ⁻⁴	-1.85	3	4.6·10 ⁻²	0.05	3	3.1·10 ⁻⁵
	1430	-6.05	3	1.3·10 ⁻³	-1.42	3	8.1·10 ⁻²	0.38	3	9.5·10 ⁻⁵
5	1300	-11.19	3	6.2·10 ⁻⁶	-3.26	3	8.5·10 ⁻³	-1.85	3	7.9·10 ⁻⁷
	1344	-10.94	3	8.5·10 ⁻⁶	-3.30	3	9.5·10 ⁻³	-2.27	3	1.3·10 ⁻⁶
	1387	-9.14	6	5.5·10 ⁻⁵	-2.73	6	1.9·10 ⁻²	-1.77	6	5.0·10 ⁻⁶
	1430	-8.82	3	7.9·10 ⁻⁵	-2.68	3	2.3·10 ⁻²	-1.90	3	9.7·10 ⁻⁶
	1455	-9.02	1	6.7·10 ⁻⁵	-2.79	1	2.2·10 ⁻²	-2.14	1	1.2·10 ⁻⁵

FIGURE LEGEND

Fig. 1. Experimental partial pressures of oxygen (- Expt 1,
- Expt 2, - Expt 3) over V_3O_5 and literature data
for oxygen pressures in heterogeneous regions
 V_2O_{3+x}/V_3O_5 and V_3O_5/V_4O_7 (from reference 24,
from references 27,30)

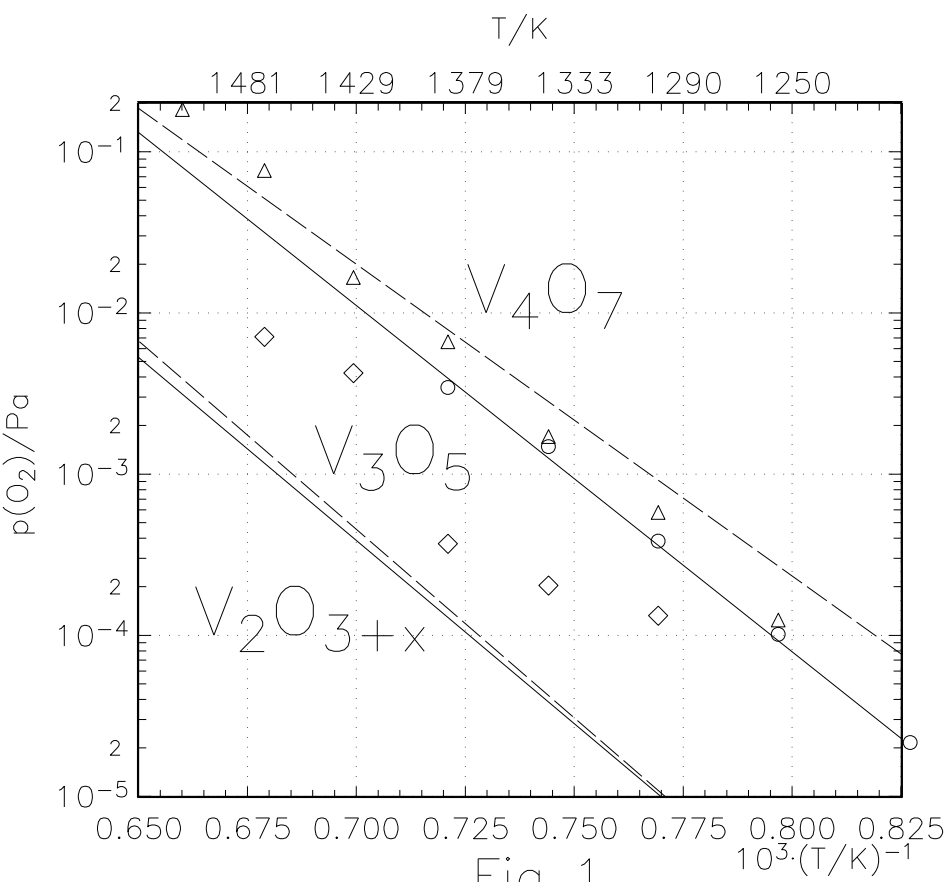


Fig. 1