

DETERMINATION OF THE ELECTRON AFFINITY OF  $\text{PtO}_2^-$  BY THE  
METHOD OF IONIC-MOLECULAR EQUILIBRIUME. B. Rudnyi, O. V. Kuznetsova,  
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*The Knudsen effusion method is used in conjunction with mass-spectral recording of negative ions to measure the equilibrium constants of reactions involving  $\text{PtO}_2^-$ . The heats of formation  $\Delta_f H_0^0(\text{PtO}_2^-) = -66 \pm 18 \text{ kJ/mole}$  and electron affinity  $EA(\text{PtO}_2^-) = 262 \pm 19 \text{ kJ/mole}$  are determined.*

The present study was undertaken to record the negative ion  $\text{PtO}_2^-$  in order to investigate negative oxygen-containing ions of tungsten [1]. We formed  $\text{PtO}_2^-$  during the vaporization of the system  $\text{Na}_2\text{WO}_4\text{--Na}_2\text{SO}_4$  from a platinum crucible at 1255–1430 K. As the other negative ions,  $\text{PtO}_2^-$  was formed inside a Knudsen effusion chamber and was in equilibrium with the condensed phases. The formation of  $\text{PtO}_2^-$  can be connected with the fact that relatively high oxygen and electron pressures were created in the experiment. Investigators previously observed  $\text{PtO}_2^-$  with the use of secondary ion–ion emission [2] and electric discharge [3]. The thermodynamic properties of  $\text{PtO}_2^-$  are unknown. Gas-phase molecules of  $\text{PtO}_2$  are formed during the oxidation of platinum by oxygen [4–9], and the Gibbs energy has been reliably determined for it.

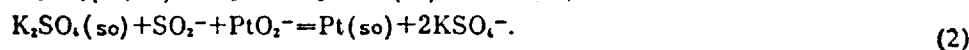
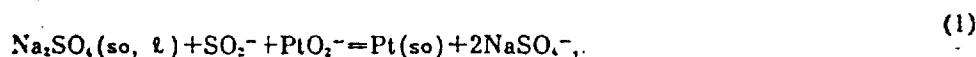
The goal of our study is to determine the heat of formation of the negative ion  $\text{PtO}_2^-$  and the electron affinity of  $\text{PtO}_2^-$ .

**Experiment.** The study was conducted using an MKh-1303 mass spectrometer (60°, 200 mm) modified for studying ionic-molecular equilibria [10]. The investigated systems were vaporized from a platinum crucible 12 mm in diameter and 12 mm in height. The diameter of the effusion hole was 0.3–0.8 mm. Temperature was measured with a Pt–Pt/Rh (10%) thermocouple. The temperature measurement error was  $\pm 3 \text{ K}$ . The ion currents were recorded with a VEU-6 channel-type electron multiplier.

**Measurement of Equilibrium Constants with the Participation of  $\text{PtO}_2^-$ .** The negative ion  $\text{PtO}_2^-$  was observed during vaporization of the systems  $(x\text{Na}_2\text{WO}_4 + (1-x)\text{Na}_2\text{SO}_4)$  ( $x = 0.17$  and  $0.97$ ), potassium sulfate, and the system  $\text{NiO--K}_2\text{SO}_4$ . The negative ions that were recorded are shown in Table 1.

The ion  $\text{PtO}_2^-$  was observed as a by-product in vapors of the system  $\text{Na}_2\text{WO}_4\text{--Na}_2\text{SO}_4$ . Results pertaining to tungsten-containing negative ions were reported in [11]. In order to more reliably determine the heat of formation of  $\text{PtO}_2^-$ , we conducted an experiment involving the vaporization of potassium sulfate. A similar experiment was conducted in [10], but the ion  $\text{PtO}_2^-$  was not given special attention. The ion  $\text{PtO}_2^-$  has also been observed in the vaporization of the system  $\text{NiO--K}_2\text{SO}_4$ . This experiment was conducted to determine the heat of formation of  $\text{NiO}_2^-$ . The results obtained for the ion  $\text{NiO}_2^-$  will be described in a separate publication.

We measured the equilibrium constants of the reactions



Unless otherwise stated, the substance participated in the reaction in the gaseous state.

TABLE 1. Mass Spectra of Negative Ions

| Number of exp. | System   | Ion (rel. intensity)*  |
|----------------|--|--|
| 1              | 0.17Na <sub>2</sub> WO <sub>4</sub> -<br>- 0.53Na <sub>2</sub> SO <sub>4</sub><br>1130 K | SO <sub>2</sub> <sup>-</sup> (100), SO <sub>3</sub> <sup>-</sup> (1000), SO <sub>4</sub> <sup>-</sup> (120), NaSO <sub>4</sub> <sup>-</sup> (722), WO <sub>3</sub> <sup>-</sup> (0.22), WO <sub>4</sub> <sup>-</sup> (3.0), NaWO <sub>4</sub> <sup>-</sup> (140), Na <sub>3</sub> S <sub>2</sub> O <sub>8</sub> <sup>-</sup> (110), Na <sub>3</sub> SWO <sub>8</sub> <sup>-</sup> (26), PtO <sub>2</sub> <sup>-</sup> (53) |
| 2              | 0.97Na <sub>2</sub> WO <sub>4</sub> -<br>- 0.03Na <sub>2</sub> SO <sub>4</sub><br>1387 K | SO <sub>2</sub> <sup>-</sup> (32), SO <sub>3</sub> <sup>-</sup> (290), SO <sub>4</sub> <sup>-</sup> (29), NaSO <sub>4</sub> <sup>-</sup> (47), WO <sub>3</sub> <sup>-</sup> (5.5), WO <sub>4</sub> <sup>-</sup> (42), NaWO <sub>4</sub> <sup>-</sup> (1000), Na <sub>3</sub> SWO <sub>8</sub> <sup>-</sup> (7.1), PtO <sub>2</sub> <sup>-</sup> (19)   |
| 3              | K <sub>2</sub> SO <sub>4</sub><br>1308 K   | SO <sub>2</sub> <sup>-</sup> (480), SO <sub>3</sub> <sup>-</sup> (1000), SO <sub>4</sub> <sup>-</sup> (23), KSO <sub>4</sub> <sup>-</sup> (780), K <sub>3</sub> S <sub>2</sub> O <sub>8</sub> <sup>-</sup> (19), PtO <sub>2</sub> <sup>-</sup> (14)  |
| 4              | NiO - K <sub>2</sub> SO <sub>4</sub><br>1300 K   | SO <sub>2</sub> <sup>-</sup> (730), SO <sub>3</sub> <sup>-</sup> (1000), SO <sub>4</sub> <sup>-</sup> (12), KSO <sub>4</sub> <sup>-</sup> (500), K <sub>3</sub> S <sub>2</sub> O <sub>8</sub> <sup>-</sup> (12), PtO <sub>2</sub> <sup>-</sup> (2.7), NiO <sub>2</sub> <sup>-</sup> (40)   |

\*Ion currents measured with an electron multiplier are shown. The ion current of the isotope with the mass number 227 is shown for PtO<sub>2</sub><sup>-</sup>, while the values shown for the sulfur-, tungsten-, and potassium-containing ions correspond to the isotopes <sup>32</sup>S, <sup>186</sup>W, and <sup>39</sup>K, respectively.

TABLE 2. Experimental Values of the Equilibrium Constants of Reaction (1)

| Number of expt. | T, K | ln K <sub>1</sub> <sup>a</sup> | i <sup>**</sup> | n <sub>1</sub> <sup>***</sup> | ln K <sub>p(1)</sub> | ΔH <sub>1</sub> <sup>a</sup> (1),<br>kJ/mole | α (Na <sub>2</sub> SO <sub>4</sub> ) |
|-----------------|------|--------------------------------|-----------------|-------------------------------|----------------------|--|--------------------------------------|
| 1               | 1344 | 7.04                           | -               | 1                             | 4.43                 | -109.6                                       | 0.66                                 |
|                 | 1387 | 6.54                           | 0.17            | 3                             | 3.90                 | -109.6                                       | 0.68                                 |
|                 | 1430 | 5.87                           | 0.19            | 2                             | 3.20                 | -107.2                                       | 0.78                                 |
| 2               | 1387 | 6.63                           | 0.23            | 5                             | 4.13                 | -112.2                                       | 0.025                                |
|                 | 1413 | 6.46                           | 0.05            | 2                             | 3.93                 | -113.5                                       | 0.030                                |

\*For experiment 1,  $\ln K_1 = \ln [I(\text{NaSO}_4^-)^3 / I(\text{PtO}_2^-) I(\text{SO}_2^-) \times I(\text{Na}_3\text{S}_2\text{O}_8^-)]$ ; for experiment 2,  $\ln K_1 = \ln [I(\text{NaSO}_4^-)^2 \times I(\text{NaWO}_4^-) / I(\text{PtO}_2^-) I(\text{SO}_2^-) I(\text{Na}_3\text{SWO}_8^-)]$ .

TABLE 3. Experimental Values of the Equilibrium Constant of Reaction (2)

| Number of expt. | T, K | ln K <sub>1</sub> <sup>a</sup> | i <sup>**</sup> | n <sub>1</sub> | ln K <sub>p(2)</sub> | ΔH <sub>1</sub> <sup>a</sup> (2),<br>kJ/mole | α (K <sub>2</sub> SO <sub>4</sub> ) |
|-----------------|------|--------------------------------|-----------------|----------------|----------------------|--|-------------------------------------|
| 3               | 1237 | 4.87                           | 0.10            | 2              | 4.20                 | -84.4  | 1                                   |
|                 | 1282 | 5.01                           | 0.18            | 3              | 4.34                 | -90.7  | 1                                   |
|                 | 1291 | 4.37                           | 0.08            | 3              | 3.80                 | -86.0  | 1                                   |
|                 | 1308 | 4.58                           | 0.12            | 2              | 3.92                 | -89.1  | 1                                   |
|                 | 1326 | 4.99                           | 0.22            | 5              | 4.33                 | -95.6  | 1                                   |
| 4               | 1210 | 9.14                           | 0.01            | 2              | 4.82                 | -87.7  | 0.63                                |
|                 | 1255 | 8.85                           | 0.37            | 3              | 4.60                 | -90.4  | 0.64                                |
|                 | 1300 | 8.56                           | 0.06            | 2              | 4.38                 | -93.2  | 0.81                                |
|                 | 1328 | 8.45                           | 0.19            | 2              | 4.32                 | -95.7  | 0.65                                |

\*For experiment 3,  $\ln K_1 = \ln [I(\text{KSO}_4^-)^2 / I(\text{PtO}_2^-) I(\text{SO}_2^-)]$ ; for experiment 4,  $\ln K_1 = \ln [I(\text{KSO}_4^-)^3 / I(\text{PtO}_2^-) I(\text{SO}_2^-) I(\text{K}_3\text{S}_2\text{O}_8^-)]$ .

TABLE 4. Thermodynamic Functions of  $\text{PtO}_2$  and  $\text{PtO}_2^-$ 

| T, K | $\text{PtO}_2^-$   |                               | $\text{PtO}_2$     |                               |
|------|--------------------|-------------------------------|--------------------|-------------------------------|
|      | $q_r$ , J/(mole·K) | $H^\circ - H^\circ$ , kJ/mole | $q_r$ , J/(mole·K) | $H^\circ - H^\circ$ , kJ/mole |
| 298  | 243.3              | 11.1                          | 237.5              | 11.1                          |
| 400  | 254.6              | 15.9                          | 248.8              | 15.9                          |
| 600  | 271.5              | 26.1                          | 265.7              | 26.1                          |
| 800  | 294.4              | 37.0                          | 278.6              | 37.0                          |
| 1000 | 297.9              | 48.1                          | 289.2              | 48.1                          |
| 1200 | 303.8              | 59.4                          | 298.1              | 59.1                          |
| 1400 | 311.5              | 70.8                          | 305.8              | 70.8                          |
| 1600 | 318.3              | 82.3                          | 312.6              | 82.3                          |
| 1800 | 324.4              | 93.8                          | 318.7              | 93.8                          |
| 2000 | 330.0              | 105.3                         | 324.2              | 105.3                         |

TABLE 5. Initial Thermodynamic Quantities

| Compound                               | $\Delta_f H^\circ$ , kJ/mole | $\Phi_{1000}^\circ$ , J/(mole·K) | $\Phi_{1200}^\circ$ , J/(mole·K) | $\Phi_{1400}^\circ$ , J/(mole·K) |
|--|------------------------------|----------------------------------|----------------------------------|----------------------------------|
| $\text{Na}_2\text{SO}_4$ (so. l.) [23] | -1376.4±0.4                  |                                  | 246.8±1.5                        | 275.7                            |
| $\text{K}_2\text{SO}_4$ (so. l.) [23]  | -1427.2±0.5                  | 231.6                            | 260.8±1.6                        | -                                |
| Pt (sd) [24]                           | 0                            | 49.6                             | 54.2±0.5                         | 58.3                             |
| $\text{SO}_2^-$ [23]                   | -400.1±3.5                   | 269.3                            | 277.9±1.5                        | 285.4                            |
| $\text{NaSO}_3^-$ [11]                 | -976±13                      | 350.0                            | 367.8±7.3                        | 383.6                            |
| $\text{KSO}_3^-$ [11]                  | -992±12                      | 360.2                            | 378.1±7.8                        | 394.0                            |

TABLE 6. Heats of Formation of  $\text{PtO}_2$ 

| Literature, year | Temp. interval, K | $\Delta_f H^\circ$ (II) *, kJ/mole | $\Delta_f H^\circ$ (III) *, kJ/mole |
|------------------|-------------------|------------------------------------|-------------------------------------|
| [4], 1960        | 1398-1843         | 174±5                              | 196±7                               |
| [5], 1960        | 1405-1506         | 186±5                              | 196±7                               |
| [7], 1961        | 1473-1773         | 191                                | 197±7                               |
| [8], 1967        | 1933-2018         | 172±4                              | 234±13                              |

\*The doubled standard deviation is shown as the error.

\*\*The error shown is the total error, including the errors of the thermodynamic functions used.

The equilibrium constant of the reactions (using (1) as an example) has the form

$$K_p(1) = \frac{p(\text{NaSO}_3^-) \cdot a(\text{Pt})}{p(\text{SO}_2^-) p(\text{PtO}_2^-) a(\text{Na}_2\text{SO}_4)}$$

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

$$\frac{p(A^-)}{p(B^-)} = \frac{I(A^-)}{I(B^-)} \frac{M(A^-)}{M(B^-)} \frac{i(B^-)}{i(A^-)}$$

where  $p$  is the partial pressure;  $I$  is the ion current of the isotope, measured on the multiplier;  $M$  is mass;  $i$  is the content of the measured isotope.

The activity of platinum in all of the experiments was taken equal to unity, since the vaporization occurred from a platinum crucible.

The activity of sodium sulfate in experiment I was determined using the associated negative ion  $\text{Na}_3\text{S}_2\text{O}_8^-$

$$a(\text{Na}_2\text{SO}_4) = \frac{p(\text{Na}_3\text{S}_2\text{O}_8^-)}{p(\text{NaSO}_3^-)} \frac{1}{K_p(3)}$$

where  $K_p(3)$  is the equilibrium constant of the reaction



According to [12],  $\ln K_p(3) = 1235/T - 1.672$ .

In experiment 2, the intensity of the ion  $\text{Na}_3\text{S}_2\text{O}_8^-$  was lower than the sensitivity limit and the activity of sodium sulfate was determined from the ratio of ion currents of  $\text{Na}_3\text{SWO}_8^-$  and  $\text{NaWO}_4^-$  and the equilibrium constant of the reaction



According to [1],  $\ln K_p(4) = 2990/T - 3.14$ .

In experiment 3, the activity of potassium sulfate was taken equal to unity, since potassium sulfate and platinum do not form solid solutions.

In experiment 4, the activity of potassium sulfate was determined from the ratio of the ion currents of  $\text{K}_3\text{S}_2\text{O}_8^-$  and  $\text{KSO}_4^-$  and the equilibrium constants of the reaction



According to [10],  $\ln K_p(5) = -2598/T - 0.493$ .

Inserting the expression for activity into the equilibrium constant of reactions (1) and (2) and changing over from the ratio of the partial pressures to ion currents, we obtain the following theoretical formulas

$$\ln K_p(1) = \ln \frac{I(\text{NaSO}_4^-)^2}{I(\text{PtO}_2^-)I(\text{SO}_2^-)I(\text{Na}_3\text{S}_2\text{O}_8^-)} + \ln K_p(3) - 1.896$$

for experiment 1,

$$\ln K_p(1) = \ln \frac{I(\text{NaSO}_4^-)I(\text{NaWO}_4^-)}{I(\text{PtO}_2^-)I(\text{SO}_2^-)I(\text{Na}_3\text{SWO}_8^-)} + \ln K_p(4) - 1.474$$

for experiment 2,

$$\ln K_p(2) = \ln \frac{I(\text{KSO}_4^-)^2}{I(\text{PtO}_2^-)I(\text{SO}_2^-)} - 0.662$$

for experiment 3,

$$\ln K_p(2) = \ln \frac{I(\text{KSO}_4^-)^2}{I(\text{PtO}_2^-)I(\text{SO}_2^-)I(\text{K}_3\text{S}_2\text{O}_8^-)} + \ln K_p(5) - 1.686$$

for experiment 4.

The experimental data is shown in Tables 2 and 3. For greater clarity, these tables also show values of the activity of sodium sulfate and potassium sulfate.

**Thermodynamic Functions of  $\text{PtO}_2^-$  and  $\text{PtO}_2$ .** In order to calculate the enthalpies of reaction from the equilibrium constants, it is necessary to know the corrected Gibbs energies  $\Phi^0$  of the participants in the reaction. We used the method of statistical thermodynamics in the rigid rotator — harmonic oscillator approximation to calculate  $\Phi^0$  for the molecule  $\text{PtO}_2$  and the ion  $\text{PtO}_2^-$ .

The method of infrared spectroscopy was used in [13] to study products of the reaction of group VIII elements (Ni, Pd, and Pt) with oxygen in an argon matrix. It was found that the  $\text{MO}_2$  molecules that are formed have a cyclic structure ( $C_{2v}$  symmetry), i.e., an atom of the metal is bound with a molecule of oxygen that has not undergone

complete dissociation. The authors determined the frequency of vibration of the O—O bond for the molecule (927  $\text{cm}^{-1}$ ) and, by analogy with  $\text{NiO}_2$  and  $\text{PdO}_2$  molecules, evaluated the frequency corresponding to the vibration of  $\text{Pt}-(\text{O}_2)$  ( $415^+ - 30 \text{ cm}^{-1}$ ).

A nonempirical quantum-mechanical calculation performed in [14] for the molecule  $\text{NiO}_2$  confirmed that the cyclic structure is the most stable structure (the fundamental electronic state  $^1A_1$ ,  $R(\text{Ni}-\text{O}) = 0.186 \text{ nm}$ ,  $R(\text{O}-\text{O}) = 0.14 \text{ nm}$ ).

The authors of [15-21] studied the interaction of molecular oxygen with the surface of a metal plate. They determined the frequency of vibration of adsorbed oxygen ( $875 \text{ cm}^{-1}$  [15, 16],  $830 \text{ cm}^{-1}$  [17]) and the distance  $R(\text{O}-\text{O})$  ( $0.145 \text{ nm}$  [18];  $0.132 \text{ nm}$  [19];  $0.14 \text{ nm}$  [20]).

Proceeding on the basis of the above-cited data, for the molecule  $\text{PtO}_2$  we chose a cyclic structure ( $\sigma = 2$ ,  $g_0 = 1$ ) with  $R(\text{Pt}-\text{O}) = 0.186 \text{ nm}$ ,  $R(\text{O}-\text{O}) = 0.14 \text{ nm}$  and frequencies of normal vibration  $927 \pm 15$ ,  $415 \pm 30$ ,  $700 \pm 140 \text{ cm}^{-1}$ . The last frequency was evaluated on the basis of a comparative analysis of the frequencies of normal vibration in molecules  $M(\text{O}_2)$  [22]. The product of the principal moments of inertia is equal to  $7.7 \cdot 10^{-115} \text{ g}^3 \cdot \text{cm}^6$ . Its error is estimated to be  $\pm 60\%$ . Excited electronic states were not considered. It is understood that the negative ion  $\text{PtO}_2^-$  also has molecular states apart from the degeneracy of the fundamental electronic state ( $g_0 = 2$ ).

Table 4 shows calculated values of  $\Phi^0$  and  $H^0 - H'_0{}^0$ . The error of  $\Phi^0$  was calculated in accordance with the law of propagation of errors from the errors of the principal moments of inertia, the frequencies of the normal vibrations ( $\pm 20\%$  for all frequencies in the case of  $\text{PtO}_2^-$ ), and the rigid rotator — harmonic oscillator approximation (5% of the oscillatory component of  $\Phi^0$  [23]). It was found that  $\Phi^0$  has an error of  $4.5 \text{ J}/(\text{mole} \cdot \text{K})$  for  $\text{PtO}_2$  at  $1200 \text{ K}$  and  $4.9 \text{ J}/(\text{mole} \cdot \text{K})$  for  $\text{PtO}_2^-$  at the same temperature.

**Heat of Formation of  $\text{PtO}_2^-$ .** Using the third law of thermodynamics, we determine the heats of reaction (Tables 2 and 3) from the equilibrium constants of reactions (1) and (2) and the corrected Gibbs energies of the reactions' participants (Table 4 and 5). The mean value was  $\Delta H_0^0 = -111 \pm 22 \text{ kJ}/\text{mole}$  for reaction (2). Table 2 and 3 show the total error calculated from the error propagation law, including the reproducibility error and the error of  $\Phi^0$ . It should be noted that the error of the corrected Gibbs energies made the largest contribution to the error of the heats of reaction (80%).

In the course of using the heats of formation of the substances entering into the reactions (Table 5), we determine the heat of formation of the negative ion  $\text{PtO}_2^-$ : we obtained  $\Delta_f H_0^0 = -65 \text{ kJ}/\text{mole}$  from reaction (1) and  $\Delta_f H_0^0 = -66 \text{ kJ}/\text{mole}$  from reaction (2). We took the mean as the recommended value.

Let us determine the error of the heat of formation of  $\text{PtO}_2^-$ . The value  $\pm 34 \text{ kJ}/\text{mole}$  is obtained on the basis of the error propagation law from the total error of the heats of reaction and the error of the initial heats of formation. However, this value is too high. The heats of formation of  $\text{NaSO}_4^-$  and  $\text{KSO}_4^-$  were obtained by solving an indeterminate system of equations [11] which already included the errors of the corrected Gibbs energies, the heats of formation, and  $\Phi^0$  for  $\text{SO}_2^-$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4$ . As a result, these errors are accounted for twice when the error propagation law is used to calculate the error of the heat of formation of  $\text{PtO}_2^-$ .

In other words, the errors of the heats of formation of the initial substances (Table 5) were correlated with each other and with the errors of the corrected Gibbs energies. This correlation must be taken into account in order to correctly evaluate the heat of formation of  $\text{PtO}_2^-$ . We did this by using a simplified approach similar to that described in [11]. It is understood that the values of  $\Phi^0$  and their errors are independent of the temperature. It should also be noted that this approximation was used only to evaluate the error, not to determine the actual heat of formation of  $\text{PtO}_2^-$ .

In the given approximation, the vector of the resulting heats of formation  $\Delta_f H_B^0$  (which contains only one quantity in the given case) is the linear transformation

$$\Delta_f H_B^0 = A \{ Y + TX\Phi^0 - X_A \Delta_f H_A^0 \}$$

of the vector of the corrected Gibbs energies  $\Phi^0$ , the vector of the initial heats of formation  $\Delta_f H_A^0$ , and the vector  $Y$  obtained from the experimental equilibrium constants. The matrix  $X = (X_B, X_A)$  is the matrix containing the mean temperatures at which the experiments were conducted;  $A$  is the matrix obtained from the solution of systems of linear equations. The notation used here is described in greater detail in [11].

When we use the rules for the transformation of random vectors, we obtain an expression for the dispersion matrix of the resulting heats of formation

$$D(\Delta H_r^0) = A \{ D(Y) + TXD(\Phi^0)X^T + X_A D(\Delta H_A^0)X_A^T - \\ - X_A \text{cov}(\Delta H_A^0, \Phi^0)X^T - TX \text{cov}(\Phi^0, \Delta H_A^0)X_A^T \} A^{-1}$$

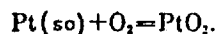
where  $D$  is the dispersion matrix; cov is the covariance matrix.

The above expression differs somewhat from Eq. (7) in [11], since it accounts for covariance between the heats of formation of the initial compounds and their corrected Gibbs energies. In [11],  $\text{cov}(\Delta_f H_A^0, \Phi^0)$  was taken equal to the zero matrix.

The value  $\pm 18$  kJ/mole was obtained when we calculated the error of the heat of formation of  $\text{PtO}_2^-$  from the above equation with allowance for the correlation.

Thus, the recommended value  $\Delta_f H_0^0(\text{PtO}_2^-) = -66 \pm 18$  kJ/mole. This value includes the total error, comprised of the reproducibility error, the error of  $\Phi^0$ , and the errors of the initial heats of formation.

**Heat of Formation and Electron Affinity of  $\text{PtO}_2^-$ .** The equilibrium constants of the formation reaction



were calculated for  $\text{PtO}_2$  in [4-9]. We used the experimental data from [4-9] to calculate the heats of reaction in accordance with the second and third laws of thermodynamics. Here, we employed new corrected Gibbs energies (Table 4). The values of  $\Phi^0$  were taken from [24] for  $\text{Pt}(\text{so})$  and from [23] for oxygen. The results are shown in Table 6.

We believe that the data obtained in [4, 5, 7] from the third law of thermodynamics is more reliable. As can be seen, it is consistent. The results obtained from the second law of thermodynamics deviate from one another by amounts greater than the accompanying error. They are thus less reliable, in our opinion.

We took  $\Delta_f H_0^0(\text{PtO}_2) = -196 \pm 7$  kJ/mole as the recommended value. This value differs somewhat from the values reported in [25] ( $171 \pm 6$  kJ/mole) and [26] (169 kJ/mole), apparently due to the use of other thermodynamic functions. Unfortunately, the method used to select the proposed values was not described in [25, 26].

The values obtained for the heats of formation of  $\text{PtO}_2^-$  and  $\text{PtO}_2$  give an electron affinity  $\text{EA}(\text{PtO}_2) = 262 \pm 19$  kJ/mole. It should be noted that this value is considerably lower than the electron affinity of  $\text{PtF}_4$  ( $\text{EA} = 531 \pm 24$  kJ/mole) [27].

Finally, let us present the dissociation energies (in kJ/mole) calculated from the values presented in this article and from handbook data:  $(\Delta_f H_0^0(\text{O})) = 246.8$ ;  $\Delta_f H_0^0(\text{O}^-) = 105.6$ ;  $\Delta_f H_0^0(\text{O}_2^-) = -42.5$  [23];  $\Delta_f H_0^0(\text{Pt}) = 564$  [24];  $\Delta_f H_0^0(\text{PtO}) = 424$  [28];  $\text{EA}(\text{Pt}) = 205$  kJ/mole [29];  $D(\text{Pt}-\text{O}) = 387$ ,  $D(\text{PtO}-\text{O}) = 475$ ,  $D(\text{Pt}-\text{O}_2) = 368$ ,  $D(\text{PtO}-\text{O}^-) = 596$ ,  $D(\text{Pt}-\text{O}_2^-) = 588$ ,  $D(\text{Pt}^--\text{O}_2) = 425$ .

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## STRUCTURE OF TEMPERATURE FIELD IN FREE-CONVECTIVE BOUNDARY LAYER AROUND VERTICAL ISOTHERMAL SURFACE

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*Experimental results on the mean and pulsational temperature values in a free-convective boundary layer around a vertical isothermal surface are outlined. Three types of flow conditions are considered: laminar, transitional, and turbulent. The features of the change in frequency spectra of the temperature pulsations in transitional flow conditions are analyzed. It is established that there is a region of repulsive force in the zone of developed turbulent flow.*

Most work on free convection has focused on the determination of the criterial laws of heat-transfer from heated surfaces. A detailed review may be found in [1]. The velocity and temperature profiles in a turbulent free-convective boundary layer were evidently first given in [2]. Only after more than 40 years [3, 4] and then in [5] were the velocity and temperature profiles in air around a vertical isothermal surface measured again. It is found, in particular, that the generalized temperature profiles are almost unchanged in the direction of the flow in turbulent conditions. This result is used to determine the end of the region of transitional conditions. Only the mean characteristics of the flow were measured in the above works.

Only a few works have reported experimental results on the pulsational characteristics and, on this basis, the structure of the free-convective flow, for example, [6, 7], where a series of interesting data on the distribution of the tangential turbulent frictional stress, the intensity of the turbulent velocity pulsations, and the temperature were obtained. In addition, in [6] much attention was paid to the transient flow conditions. As well as analysis of new results, the difficulties encountered in conducting the experiment — in particular, the high intensity level of the pulsations, the interruption of the flow, the difficulty in interpreting the thermoanemometer readings in significantly nonisothermal flows — were noted.

In [8-10], the turbulent free convection in a vertical liquid layer bounded by isothermal plates was investigated. The structure of this flow is close to a free-convective boundary layer at a vertical surface.

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