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## Abstract

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## PHYSICAL CHEMISTRY

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# EQUILIBRIUM OF LEAD TUNGSTATE WITH HYDROGEN AND THERMODYNAMIC CHARACTERISTICS OF $PbWO_4$

The equilibrium of lead tungstate was studied by means of the circulation method, described in detail in the literature ([1–6]).

Lead tungstate was prepared by precipitating a solution of $K_2WO_4$ with a solution of $Pb(CH_3COO)_2$ in stoichiometric proportions. The initial salts, of chemically pure grade, were purified beforehand by recrystallization. The precipitate of $PbWO_4$ obtained was thoroughly washed, dried, and calcined at 800–900°C. Analysis of the preparation, carried out by the method of Hillebrand and Lundell ([7]), confirmed with an accuracy of 0.5% the composition corresponding to the formula $PbWO_4$. The hydrogen for reduction was obtained by electrolysis of a 20% solution of NaOH.

A weighed amount of $PbWO_4$ in a porcelain boat was placed in a quartz reactor. The reactor was located in a tube furnace, the temperature of which was maintained constant to within ±1°. The temperature was measured with a platinum–platinum-rhodium thermocouple, previously calibrated against the melting temperatures of chemically pure metals and salts.

The water-vapor pressure was set by the temperature of a saturator with bidistilled water, placed in an ultrathermostat. The temperature of the ultrathermostat was maintained constant to within ±0.05°. The total pressure was measured with a mercury manometer to an accuracy of ±0.1 mm. The equilibrium constant was calculated from the formula $K_p = \frac{p_{H_2O}}{p_{H_2}}$. The gross composition of the reduction products was determined from the loss in weight of the preparation or from the volume of hydrogen consumed. To determine the phase composition, an X-ray study of the reduction products was carried out by the Debye method in a chamber with a diameter of 57 mm using a copper anode.

Reduction of lead tungstate proceeds in four stages:

$$10\,PbWO_4 + H_2 = 10\,PbWO_{3.9} + H_2O; \qquad \text{(I)}$$

Fig. 1. Reduction isotherms of $PbWO_4$ for temperatures: a = 675°; b = 825°

Figure 1: Fig. 1. Reduction isotherms of $PbWO_4$ for temperatures: a = 675°; b = 825°

Fig. 2. Dependence of lg Kp on 1/T for the second stage of reduction of $PbWO_4$

Figure 2: Fig. 2. Dependence of lg Kp on 1/T for the second stage of reduction of $PbWO_4$

$$^{50}/_{59}\,PbWO_{3.9} + H_2 = {}^{50}/_{59}\,Pb + {}^{50}/_{59}\,WO_{2.72} + H_2O; \qquad \text{(II)}$$

$$^{50}/_{36}\,WO_{2.72} + H_2 = {}^{50}/_{36}\,WO_2 + H_2O; \qquad \text{(III)}$$

$$^{1}/_{2}\,WO_2 + H_2 = {}^{1}/_{2}\,W + H_2O. \qquad \text{(IV)}$$

It should be noted that we regard the reduction of $PbWO_4$ to $PbWO_{3.9}$ as a stage only formally, since we take into account the corresponding segment of the isotherm when calculating the thermodynamic characteristics of $PbWO_4$. In fact, we were unable to detect any changes in the structure of the preparation when oxygen decreased by $\sim 0.1$ atom. Moreover, the equilibrium constants in this region are rather high and drop sharply with composition, which presents considerable difficulties in measuring them. Therefore this segment of the isotherm was not studied in as much detail as the others.

In calculating the total thermodynamic characteristics of the complete reduction of $PbWO_4$, the first segment can be taken into account by integrating $\lg K_{p1}$ with respect to the number of oxygen atoms $n$ in the interval $n = 4$—3.9

$$\frac{\Delta Z_1^0}{4.576T} = -\int_4^{3.9} \lg K_{p1}\, dn.$$

The low accuracy of the high values of the equilibrium constants obtained by us in the indicated interval of $n$ permits the integration to be carried out along a straight line; or, equivalently, to use the value of $K_p$ from the interpolation line for the midpoint of the interval $n$, and to replace the inclined straight line by an equivalent step.

**Fig. 1.** Reduction isotherms of $PbWO_4$ for temperatures: $a = 675°$; $b$—825°

**Fig. 2.** Dependence of $\lg K_p$ on $1/T$ for the second stage of reduction of $PbWO_4$

the straight line for the midpoint of the interval $n$, and replace the inclined straight line by an equivalent step. We take the values of $\lg K_{p1}$ for $n = 3.95$ from the straight line $\lg K_{p1} = f(n)$, constructed by graphical approximation: $t = 825°$, $\lg K_{p1} = 0.763$; $t = 675°$, $\lg K_{p1} = 0.672$.

The equation of the straight line passing through two points has the form:

$$\lg K_{p1} = -633.6T^{-1} + 1.3404. \quad (1)$$

In the second stage of reduction, metallic lead and tungsten oxide $WO_{2.72}$ are obtained; in the third and fourth stages, tungsten oxides are reduced. Table 1 gives the dependence of the constant

**Table 1**

| Gross composition of the preparation | $K_p$ at 825° | $K_p$ at 675° | Gross composition of the preparation | $K_p$ at 825° | $K_p$ at 675° |
|---|---|---|---|---|---|
| $PbWO_{3.98}$ | 10.2 | 9.9 | $PbWO_{2.72}$ | 1.38 | |
| $PbWO_{3.96}$ | 8.9 | 8.8 | $PbWO_{2.72}$ | 1.34 | |
| $PbWO_{3.95}$ | 6.5 | 4.7 | $PbWO_{2.72}$ | 1.218 | |
| $PbWO_{3.95}$ | 5.2 | 4.77 | $PbWO_{2.5}$ | 1.211 | |
| $PbWO_{3.93}$ | 4.4 | 1.76 | $PbWO_{2.25}$ | 1.209 | |
| $PbWO_{3.92}$ | 3.98 | 1.25 | $PbWO_{2.0}$ | 1.201 | 0.3520 |
| $PbWO_{3.90}$ | 3.6 | 1.06 | $PbWO_{2.0}$ | 0.7611 | 0.293 |
| $PbWO_{3.8}$ | 2.2 | 1.04 | $PbWO_{2.0}$ | 0.6365 | 0.242 |
| $PbWO_{3.5}$ | 2.1 | 1.03 | $PbWO_{2.0}$ | 0.4448 | 0.216 |
| $PbWO_{2.9}$ | 2.2 | 1.03 | $PbWO_{1.7}$ | 0.3345 | 0.1790 |
| $PbWO_{2.75}$ | 1.91 | 0.898 | $PbWO_{0.5}$ | | 0.1558 |
| $PbWO_{2.73}$ | 1.88 | 0.87 | $PbWO_{0.13}$ | 0.3394 | |
| $PbWO_{2.73}$ | 1.63 | | $PbWO_{0.1}$ | 0.3402 | |

equilibrium on the gross composition of the reduction products. This same dependence is shown in Fig. 1.

Table 2 and Fig. 2 give the temperature dependence of the equilibrium constant for the second stage of the reduction of lead tungstate.

**Table 2**

| Temp., °C | $K_p$ mean | $K_p$ calc. |
|---|---|---|
| 825 | 2.16 | 2.16 |

| Temp., °C | $K_p$ mean | $K_p$ calc. |
|---|---|---|
| 770 | 1.64 | 1.68 |
| 751 | 1.53 | 1.53 |
| 713 | 1.28 | 1.275 |
| 675 | 1.04 | 1.035 |

The data of Table 2 are represented, with an accuracy of $\pm 0.5\%$, by the equation

$$\lg K_{\mathrm{pII}} = -2227.5T^{-1} + 2.3635. \tag{2}$$

For the third and fourth stages we used the equations given in the work of I. A. Vasil' eva et al. ([6]), since our reduction data and X-ray phase-analysis data agree, within the limits of experimental error, with Vasil' eva' s data.

$$\lg K_{\mathrm{pIII}} = \lg p_{\mathrm{H_2O}}/p_{\mathrm{H_2}} = -904.83T^{-1} + 0.90642; \tag{3}$$

$$\lg K_{\mathrm{pIV}} = \lg p_{\mathrm{H_2O}}/p_{\mathrm{H_2}} = -2325T^{-1} + 1.650. \tag{4}$$

Combining equations I, II, III, and IV, we obtain for the reaction of complete reduction of $PbWO_4$:

$$\mathrm{PbWO_4} + 4\mathrm{H_2} = \mathrm{Pb_l} + \mathrm{W} + 4\mathrm{H_2O}; \tag{5}$$

$$\lg K_{\mathrm{pV}} = 0.1 \lg K_{\mathrm{pI}} + 1.18 \lg K_{\mathrm{pII}} + 0.72 \lg K_{\mathrm{pIII}} + 2 \lg K_{\mathrm{pIV}};$$

$$\lg K_{\mathrm{pV}} = -8054T^{-1} + 6.8756,$$

whence

$$\Delta Z^0_{\mathrm{V}} = 36568 - 31.4558T.$$

Combining reaction (5) with the reaction of formation of water vapor

$$\mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{H_2O}, \tag{6}$$

we obtain, for the reaction of formation of $PbWO_4$ from the elements,

$$\mathrm{Pb_l} + \mathrm{W} + 2\mathrm{O_2} = \mathrm{PbWO_4}, \tag{7}$$

$$\Delta Z^0_{\text{VII}} = 4\Delta Z^0_{\text{VI}} - \Delta Z^0_{\text{V}}.$$

For the reaction of formation of water vapor we use Chipman' s equation ([8])

$$\Delta Z^0_T = -59251 + 0.871T \ln T - 7.5 \cdot 10^{-5}T^2 + 408000T^{-1} + 6.8085T.$$

Table 3 gives the calculated values of $\Delta Z^0_{\text{V}}$, $\Delta Z^0_{\text{VII}}$, and the mean thermal effect of reaction (7) for the experimental temperatures.

**Table 3**

| Temp., °K | $\Delta Z^0_{\text{V}}$, cal/mole | $\Delta Z^0_{\text{VII}}$, cal/mole | $\Delta H^0_{\text{VII}}$, cal/mole |
|---|---|---|---|
| 973 | +5962 | −191762 | −273770 |
| 1023 | +4388 | −187648 | −273770 |
| 1073 | +2816 | −182616 | −273770 |
| 1123 | +1243 | −179123 | −273770 |

In order to calculate the thermodynamic characteristics under standard conditions for the reaction:

$$\text{Pb}_{\text{s}} + \text{W} + 2\text{O}_2 = \text{PbWO}_4, \tag{8}$$

we proceed as follows. Taking into account the temperature dependence of the heat capacity for $\text{Pb}_{\text{l}}$ and all the other participants in the reaction, we calculate the thermodynamic functions of reaction (7) for the melting temperature of lead, $T = 600.6°\text{K}$.

$$c_{p\text{Pb}_{\text{l}}} = 7.7633 - 0.73714 \cdot 10^{-3}T \quad ([12])$$

$$c_{p\text{PbWO}_4} = 28.505 + 9.412 \cdot 10^{-3}T \quad ([9])$$

$$c_{p\text{O}_2} = 7.52 + 0.81 \cdot 10^{-3}T - 0.9 \cdot 10^{5}T^{-2} \quad ([10])$$

$$c_{p\text{W}} = 5.74 + 0.76 \cdot 10^{-3}T \quad ([10])$$

For $\Delta c_p$ we have: $\Delta c_p = -0.038 + 7.769 \cdot 10^{-3}T + 1.8 \cdot 10^{5}T^{-2}$.

Consequently: $\Delta H^0_T = \Delta H_0 - 0.038T + 3.884 \cdot 10^{-3}T^2 - 1.8 \cdot 10^{5}T^{-1}$.

Substituting the experimentally found $\Delta H_T^0 = -273770$ for the mean temperature of the experiments $T = 1048°\text{K}$, we find $\Delta H_0 = -277824$. Next, we write the expression for $\Delta Z_T^0$:

$$\Delta Z_T^0 = -277824 + 0.038\,T \ln T - 3.884 \cdot 10^{-3} T^2 - 0.9 \cdot 10^5 T^{-1} + IT,$$

where $I$ is the integration constant, which we determine by substituting several experimental values of $\Delta Z_T^0$. We obtain $I_{\text{mean}} = 92.19$.

Thus, for reaction (7) at $T = 600.6°\text{K}$, we obtain:

$$\Delta Z_{600.6}^0 = -223734 \text{ cal/mol}; \quad \Delta H_{600.6}^0 = -276746 \text{ cal/mol}; \quad \Delta S_{600.6}^0 = \\ = -88.26 \text{ cal/mol} \cdot \text{deg}.$$

We pass to $\text{Pb}_{\text{tv}}$, taking from (11) for melting $\Delta H = 1220$ cal/mol; $\Delta S = 2.03$ cal/mol $\cdot$ deg.

For reaction (8) at 600.6°K we obtain $\Delta H_{600.6}^0 = -275526$ cal/mol; $\Delta S_{600.6}^0 = -86.23$ cal/mol $\cdot$ deg; $\Delta Z_{600.6}^0 = -223734$ cal/mol.

Now we pass to the temperature 298°K. The heat capacity of all participants in the reaction, except $\text{Pb}_{\text{tv}}$, remains the same. For $\text{Pb}_{\text{tv}}$ we take

$$c_{p\text{Pb}_{\text{tv}}} = 5.640 + 2.30 \cdot 10^{-3} T \qquad (^{12}).$$

The subsequent calculation was carried out according to the scheme given above. As a result, for $\text{PbWO}_4$ we have: $\Delta Z_{298}^0 = -250.0$ kcal/mol; $\Delta H_{298}^0 = -277.0$ kcal/mol; $\Delta S_{298}^0 = -89.48$ cal/mol $\cdot$ deg.

Taking the entropies of the participants in the reaction $\text{Pb}_{\text{tv}}$: $S_{298}^0 = 15.51$ ($^{10}$); W: $S_{298}^0 = 8.00$ ($^{10}$); $\text{O}_2$: $S_{298}^0 = 49.00$ ($^{10}$).

We obtain for $\text{PbWO}_4$: $S_{298}^0 = 32.03$ cal/mol $\cdot$ deg.

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*Note: Figure translations are in progress. See original paper for figures.*