Thermogravimetric Study of the Tungsten-Oxygen System in the Range 2.89 < O/W < 3.00 between 1023 and 1223 K

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Abstract

Measurements of the partial pressure of oxygen (P_{O_2}) in the tungsten-oxygen system have been performed by a thermogravimetric technique in the composition range $2.89 < O/W < 3.00$ between 1023 and 1223 K.

Measurements at 1123 K show a substantial hysteresis of P_{O_2} as a function of composition. In spite of this undesirable effect useful thermodynamic Information on the nature of the phase diagram could be extracted. The homogeneity range of the WO_{3-x} phase has been determined to be $2.99 < O/W < 3.00$. With P_{O_2} decreasing, a compound has been detected around $O/W = 2.8975$ corresponding to the $W_{20}O_{58}$ phase. When the P_{O_2} is increased over 5.82×10^{-12} kPa, $W_{20}O_{58}$ is oxidized indicating the formation of an intermediate phase of composition close to $O/W = 2.975$, whose stability is confined to only a short range of P_{O_2}.

The partial molar entropy and enthalpy of solution of oxygen in the WO_{3-x} phase have also been evaluated and discussed.

Introduction

The thermodynamic, crystallographic and transport properties of the tungsten-oxygen (W-O) system in the composition range $2.89 < O/W < 3.00$ have been object of several studies. From the structural point of view, this is a very interesting composition range due to the possible existence of discrete homologous series (1), also called Magnéli phases W_nO_{3n-1} and W_nO_{3n-2}. These phases are derived from the parent structure of WO_3 through crystallographic shear (CS) along {102} and {103} planes (1,2), respectively. Slight oxygen deficiency can be accomodated through {102} CS originating the W_nO_{3n-1} series, whereas further oxygen loss can be accomodated through {103} CS originating the W_nO_{3n-2} series (3,4).

The phases corresponding to W_nO_{3n-1} series have been called α'. One of them, with $n = 25$ ($O/W = 2.96$), has been characterized by Gebert and Ackermann (5). Other members of this series have been identified by high resolution transmission electron microscopy (HRTEM) studies (6).

The $W_{20}O_{58}$ was the first known and characterized phase of the W_nO_{3n-2} series (7). Other members of this series such as $W_{24}O_{70}$, $W_{25}O_{73}$, $W_{40}O_{118}$ and $W_{50}O_{148}$ have been characterized later (5,8-10) through X- ray diffraction and HRTEM studies.

For the WO_{3-x} phase there are several different propositions respect to its homogeneity range. Authors (11,12) proposed the existence of a single phase between WO_3 and $WO_{2.9873}$, whereas others (5,13) found a homogeneity range from WO_3 to $WO_{2.980}$. The existence of seven Magnéli type phases at 1023 K in the composition range $2.96 < O/W$ 3.00, as detected through electrical

resistivity measurements, have also been suggested (14). Marucco et al. (15), through thermogravimetric measurements at 1023 K under controlled P_{O_2}, determined for the homogeneity range boundary the value O/W = 2.9760. These authors, through EMF measurements, found an abrupt change of the partial molar entropy and partial molar entalphy at around the composition O/W = 2.9880. This change of the partial molar quantities is atributed (16) to a sharp change of the defect structure around of O/W = 2.9880 composition. Thus, for the composition range 2.9880 < O/W < 3.0000 the authors suggested the presence of single ionized vacancies and for the range 2.9760 < O/W < 2.9880 the existence of {102} CS type defects.

In view of the posible existence of several phases in the composition range 2.89 < O/W < 3.00 and the disagreement existing regarding the composition width of WO_{3-x} phase, in the present work we investigate the nature of the phase diagram at a convenient working temperature, namely 1123 K. The aim of this study was also to determine the stability range of WO_{3-x} phase as a function of temperature as well as the oxygen partial molar properties. This work was performed using a high sensitivity thermogravimetric equipment (17).

Experimental

The construction, details and perfomance of the experimental equipment used in our thermogravimetric measurements were described in detail elsewhere (17). In essence, this equipment consists of a symmetrical thermobalance coupled to an electrochemical system for the measurement and regulation of P_{O_2}.

The thermobalance was built on the basis of a Cahn 1000 electrobalance that allows to determine weight changes within ±10 μg at 1273 K and 10^2 kPa of total pressure. So, for our samples of about 1.5 g. of WO_3, it was possible to determine changes in O/W ratio within ± 1 x 10^{-4}.

The electrochemical system for the measurement and regulation of P_{O_2} consists of a zirconia oxygen pump and a zirconia oxygen sensor. The zirconia oxygen pump allows to control the P_{O_2} which is determined by means of the zirconia oxygen sensor. Thus, P_{O_2} can be varied from 10^2 kPa up to 10^{-25} kPa at 1073 K, using Ar, CO_2 and H_2 as gas sources (18). The errors in P_{O_2} in the mixtures can be estimated in ± 2 %, including systematic ones (18). P_{O_2} ranging between 10^2 and 1x10^{-4} kPa were obtained by means of Ar-O_2 mixtures, whereas the range of low P_{O_2} were obtained with CO-CO_2 mixtures. The gas flowrates were of 100 cm^3/min..

The P_{O_2} values at the sample temperature were calculated from the CO_2/CO ratio determined by means of the oxygen sensor and the ΔG^0 value of the reaction CO + 1/2 O_2 = CO_2 (19). The equilibrium times varied significantly with temperature and the ratio P_{CO_2}/P_{CO} ranging from a few hours up to some days.

The equilibrium criterium used in this work was "constant sample weight with time, within ± 10 μg". This equilibriun criterium was verified over periods of 24 hours.

The original material for our W-O samples was powdered WO_3 provided by SPEX Laboratories (USA), with a total impurity content of less than 200 ppm in weight (main impurities are Na, As, Si and Fe).

The measurements were performed in the temperature range 1023 < T < 1223 K. This range of temperatures was selected considering that at temperatures higher than 1223 K the vaporization rate of WO_3 is appreciable. At 1273 K we measured a rate of 50 μg daily. At 1223 K and lower temperatures this rate is neglegible and not significative mass loss was detected during the time of measurement. At temperatures of 1023 K and lower the equilibrium time increases appreciably. We observe also some problems of reproductibility of compositions under oxidation and reduction conditions, which we will discuss later on.

The absolute oxygen content of the W-O samples was determined assuming the stoichiometric ratio O/W = 3.0000 at 1023 < T < 1223 K under 10^2 kPa of oxygen. This stoichiometric reference was verified within 3.0000 ± 0.0005 reducing a sample to metallic W at 1173 K in dry hydrogen.

Prior to performing the equilibrium P_{O_2} measurements of the W-O system, the perfomance of our thermogravimetric equipment when working with low P_{O_2} was checked against the measured equilibrium P_{O_2} values of Uranium-Oxygen (U-O) system at 1173 K within the composition range 2.00 < O/U < 2.14. For this system does exist in the literature realiable data by Thomas et al (20) which were accepted as standard values. Fig. 1 shows our equilibrium P_{O_2} values for U-O compared with those of Thomas et al (20). The absolute oxygen content for the U-O samples was determined assuming the composition O/U = 2.0000 at 1173 K in dry hydrogen (20). The maximun scatter in $\log_{10} P_{O_2}$ between our data and those of Thomas et al. (20) is around 0.1.

The range of P_{CO_2}/P_{CO} ratio of the gas mixtures used in this

measurements overlap those to be measured in the W-O system. Therefore, we judged that our experimetal system would allow to perform accurate equilibrium P_{O_2} measurements in this system, in the low P_{O_2} range, at high temperatures.

Results and Discussion

Isotherm at 1123 K

This isotherm is represented in fig. 2 and its different parts are described below.

Part A-B. The sample was first annealed in pure oxygen at 1123 K during two days. Then, the starting point A shown in fig. 2 of composition O/W = 3.0000, was obtained. For P_{O_2} values corresponding to Ar-O_2 mixtures, that is $10^{-4} < P_{O_2} < 10^{2}$ kPa, no detectable change was observed in the composition of the sample. When CO-CO_2 mixtures were used, that is for P_{O_2} values lower than 10^{-8} kPa, a slight reduction of the sample was detected. Part A-B was perfectly reproducible upon oxidation (reduction) and subsequent reduction (oxidation). Therefore, it must be considered to constitute stable equilibrium states of the W-O system. Point B of this isotherm corresponds to a $P_{O_2} = 5.69 \times 10^{-12}$ kPa and a composition O/W = 2.9907.

Part B-C. When P_{O_2} was slightly lowered below the value

corresponding to point B, and for P_{O_2} = 4.05x10^{-12} kPa, the sample became unstable and began to reduce slowly. Equilibrium was not reached even after several weeks. In order to increase the reduction kinetics P_{O_2} was temporarily lowered to 4.91x10^{-13} kPa, and then raised again to 4.05x10^{-12} kPa at intervals of O/W = 0.005. For each step the weight drift decrease as the O/W ratio decreases, and finally, for a composition O/W = 2.9424, the sample reached equilibrium. This equilibrium state is represented by point C in fig. 2 with coordinates O/W = 2.9424 , P_{O_2} = 4.05x10^{-12} kPa. The equilibrium criterium for point C was verified over three days.

Part C-D. Lowering P_{O_2} from point C successively, the equilibrium values indicated in fig. 2 were obtained up to point D. Coordinates for point D are P_{O_2} = 7.56x10^{-14} kPa and O/W = 2.8970.

Part D-E. For P_{O_2} higher than that of point D it was observed a constant weight of the sample which corresponds to the formation of a stoichiometric compound. This is indicated in fig. 2 by part D-E. Part D-E of this isotherm was also perfectly reproducible upon oxidation (reduction) and subsequent reduction (oxidation) of the sample and it must be considered to represent stable equilibrium states of the W-O system. Point E corresponds to a P_{O_2} = 5.82x10^{-12} kPa and composition O/W = 2.8981.

Part E-F. For a P_{O_2} slightly higher than that of point E, and for P_{O_2} = 1x10^{-11} kPa, the sample became unstable and began to oxidate slowly. Similar to part B-C, the sample was oxidated at intervals of O/W = 0.005 with pure CO_2. After severals days, the

equilibrium point F was obtained of coordinates P_{O_2} = $1x10^{-11}$ kPa and O/W = 2.9733.

Part F-G. Increasing P_{O_2} from the value corresponding to point F, an F-G region was observed where P_{O_2} increases appreciably with composition (see fig. 2). Point G corresponds to O/W = 2.9832 and P_{O_2} = $3.47x10^{-10}$ kPa.

Part G-H. Increasing slightly P_{O_2} from the value corresponding to point G, the sample oxidates slowly, approaching the plateau G-H, reaching a final composition of O/W = 2.9941, which is indicated in fig. 2 as point H. Coordinates for point H are P_{O_2} = $1.37x10^{-9}$ kPa and O/W = 2.9941.

Part H-I. Increasing P_{O_2} from the value corresponding to point H, the sample composition remains practically constant reaching the value O/W = 2.9979 for a P_{O_2} = 10^2 kPa. This value of composition (point I in fig.2) is slightly lower than that corresponding to the starting point A (O/W = 3.0000). In order to discard any evaporation of the sample during measurement time, this was reduced to metallic W at 1173 K in dry hydrogen and suddenly oxidated to WO_3 with an $Ar-O_2$ mixture of P_{O_2} = 2 kPa. After this treatment, the sample recovered the composition O/W = 3.0000 corresponding to point A.

This 1123 K isotherm shows a substantial hysteresis in the behaviour of P_{O_2} as a function of composition, but in spite of this undesirable effect, useful information on the W-O system can be obtained.

Part A-B corresponds to the stability range of WO_{3-x} phase.

This phase is stable at 1123 K within $2.990 < O/W < 3.000$.

In spite of the values measured around $O/W = 2.94$, it is difficult to assert if point C really corresponds or not to a stable phase. In any case we think that point C belongs to an intermediate phase of marginal stability, and then very difficult to detect.

The existence of a stoichiometric compound around $O/W = 2.8975$ is indicated by part D-E. This value of composition close to 2.9000 corresponds to $W_{20}O_{58}$ phase (7).

The increase of P_{O_2} from point F to point G around $O/W = 2.975$, seems to indicate the existence of a phase, probably one of the α' phases corresponding to $n = 40$ in the series W_nO_{3n-1}. This observation agrees with that of Marucco et al (21), who found a compound of average composition $O/W = 2.975$, through the oxidation of $W_{20}O_{58}$ at 1273 K with a CO/CO_2 mixture. Part E-F would correspond to the coexistence of two phases, $W_{20}O_{58}$ and $WO_{2.975}$.

The values between points G and H seem to indicate the existence of a two phase field region, where $WO_{2.975}$ would coexist with WO_3.

The values of region H-I, which do not agree with part A-B, show that it is difficult to obtain pure WO_3 by oxidation from $W_{20}O_{58}$. The sample would be constituted mainly of WO_3 and $WO_{2.975}$ phase which coexist in a metastable way. These metastable states persist even increasing P_{O_2} to 10^2 kPa. In order to reobtain pure WO_3 we found it necessary to reduce the sample to metallic W and then suddenly reoxidate it. In this way metallic W can be oxidated directly to WO_3 avoiding the formation of intermediate phases and metastable states of lower average composition than that of point

A. The existence of this type of méatestable equilibrium states, obtained upon oxidation of a reduced phase, have been already observed in other M-O systems (22-26).

The existence of hysteresis is associated to the presence of two phases with close structural relationship between them (23-25,27-29). This relationship is satisfied by the W-O system in this range of composition due to the possible existence of the Magnéli type phases. In this case, the sample would be constituted by domains of each phase intergrown between them.

Intergrowth between {102}CS and {103}CS structures have been observed by Berglund and Sahle (4) in the system W-O. These authors, through HRTEM, studied samples prepared by reduction of WO_3 at 1270 K with CO-CO_2 mixtures. They observed the presence of paralel {102}CS structures for compositions between O/W = 2.982 and O/W = 2.977, the existence of intergrowth between {102} CS and {103}CS structures for compositions lower than O/W = 2.963, and pure {103}CS structures for compositions close to O/W = 2.900.

Our measurementes have not confirmed the existence of $WO_{2.96}$ phase reported by Gebert and Ackermann (5), which is in agreement with Marucco et al. (21).

In our measurements the $WO_{2.975}$ phase could only be obtained by oxidation from $W_{20}O_{58}$.

The existence of hysteresis in the region $2.97 < O/W < 3.00$ explains the disagreement between different authors respect to the homogeneity range of WO_{3-x} phase.

Homogeneity Range of WO_{3-x} Phase between 1023 and 1223 K

In addition to the measurements performed at 1123 K, the equilibrium P_{O_2} values at 1023, 1073, 1174 and 1123 K have been determined in the composition range $2.99 < O/W < 3.00$. In fig. 3 are shown the equilibrium P_{O_2} values obtained at 1174 K using $CO-CO_2$ mixtures. Similarly to that observed at 1123 K (fig. 2), for P_{O_2} slightly lower than that corresponding to point P (O/W = 2.9905) the sample became unstable and began to reduce slowly indicating the precipitation of a reduced phase. Similar behaviour was observed at 1023, 1073 and 1223 K. We see that the WO_{3-x} phase is stable in the composition range $2.990 < O/W < 3.000$ at temperatures between 1023 and 1223 K. This range of solubility agrees within experimental error with that determined by Sienko and Berak (11,12). However, disagreement with the results of Marucco and Htiwech (15) is found. These authors found through thermogravimetric measurements under controled P_{O_2}, a single phase between WO_3 and $WO_{2.978}$ at 1023 K. Also, using EMF measurements, they (15) observed a change of the slope of EMF values vs. 1/T around the composition O/W = 2.9880. The authors attributed this change in the partial molar entropy of oxygen to a change in the nature of defects (16), but we think that it is indicative of a first order phase transition, and corresponds to the precipitation of a reduced phase. Therefore, for O/W compositions lower than 2.9900 we are in presence of a two phase field, where WO_{3-x} coexists with a reduced phase, represented by part B-C (see fig. 2). The reasons why these authors (15) did not observe the presence of a two phase field in their thermogravimetric

measurements for O/W values lower than 2.9900 at 1023 K are not evident to the present author.

In fig. 4 are plotted $\log_{10} P_{O_2}$ vs. $\log_{10} x$ values at 1023, 1073, 1123, 1174 and 1223 K. In the range $-2.6 < \log_{10} x < -2.0$, for each temperature, the points are lined on a straight line whose slope is approximately -1/5 (as is shown in fig 4). For $\log_{10} x$ lower than -2.6 the points show a deviation of the straight line which increases as $\log_{10} x$ decreases. The linearity between $\log_{10} P_{O_2}$ and $\log_{10} x$ can be attributed to a single type of defect in dilute solution (30) and the deviation for $\log_{10} x$ values lower than -2.6 may be caused by intrinsic defects or impurities present in the sample. Also, it must be considered that the uncertainties in the compositions increase near O/W = 3.0000.

The relative partial molar entalphy and entropy of solution of oxygen in the WO_{3-x} phase were calculated in the range of linearity of $\log_{10} P_{O_2}$ vs. $\log_{10} x$. The experimental values of $\Delta\bar{G}_{O_2} = RT \text{ Ln } P_{O_2}$ were adjusted by a straight line in this range of composition. The correlation coeficients of this linear fitting for the five temperatures were higher than 0.998. Thus, it was possible to compute $\Delta\bar{G}_{O_2}$ values as a function of temperature for various intermediate compositions, and the results obtained are plotted in fig. 5.

It is observed that $\Delta\bar{G}_{O_2}$ at constant O/W has a linear variation with T between 1073 and 1223 K. The values of the partial molar properties $\Delta\bar{S}_{O_2}$ and $\Delta\bar{H}_{O_2}$ were also computed for the temperature range $1073 < T < 1223$ K and the obtained values as a function of composition are listed in Table 1. Both molar quantities show a linear variation with $\log_{10} x$.

We observed a certain irreproducibility in the values obtained at 1023 K and typical values are plotted in fig. 4 and fig. 5. A deviation from the linear behaviour of oxygen chemical potential as function of temperature seems to occur at this temperature. This may be related to the orthorhombic-tetragonal transition of WO_3 phase which takes place at temperatures somewhere between 983 and 1043 K (3,31,32). This transformation involves metastable states, as established in a careful study performed by Ackermann and Sorrell (32) on the thermal expansion and orthorhombic-tetragonal transition of the WO_3 phase. By means of X-ray diffraction at high temperatures these authors proved that this phase transition occurs in the temperature range 983-1043 K with a reproducible hysteresis between heating and cooling processes.

Comments on the Defect Structure of the WO_{3-x} Phase

Finally we will examine the implications of our measurements on the probable defect structure of the WO_{3-x} phase.

The slope of $\log_{10} P_{O_2}$ vs $\log_{10} x$ is approximately -1/5. The mass-action law (30,33,34) predicts a slope of -1/4 for single ionized vacancies and -1/6 for double ionized vacancies. The slope of -1/5 can be rationalized considering a combination of singly and doubly ionized oxygen vacancies (34,35), or other defect structures as quadruply ionized oxygen divacancies (34,36), quadruply ionized metal interstitials (34) or complex defects involving oxygen vacancies and oxygen interstitials (33).

From an alternative point of view, Panlener et al. (34)

interpreted the slope of -1/5 in $\log_{10} P_{O_2}$ vs. $\log_{10} x$ found in CeO_{2-x} assuming random configurational entropy and interacting defects. Thus, this interaction is responsible for a composition dependent $\Delta\bar{H}_{O_2}$.

In our case, $\Delta\bar{H}_{O_2}$ varies slightly with composition and the slope of $\Delta\bar{S}_{O_2}$ vs. $\log_{10} x$ is close to 4R. We consider that this variation of $\Delta\bar{H}_{O_2}$ is in fact indicative of an interaction between defects and the slope 4R of $\Delta\bar{S}_{O_2}$ vs. $\log_{10} x$ suggests the existence of random single ionized oxygen vacancies (30,34). Then, we propose for the defect structure of WO_{3-x}, the existence of random single ionized oxygen vacancies.

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Figure captions

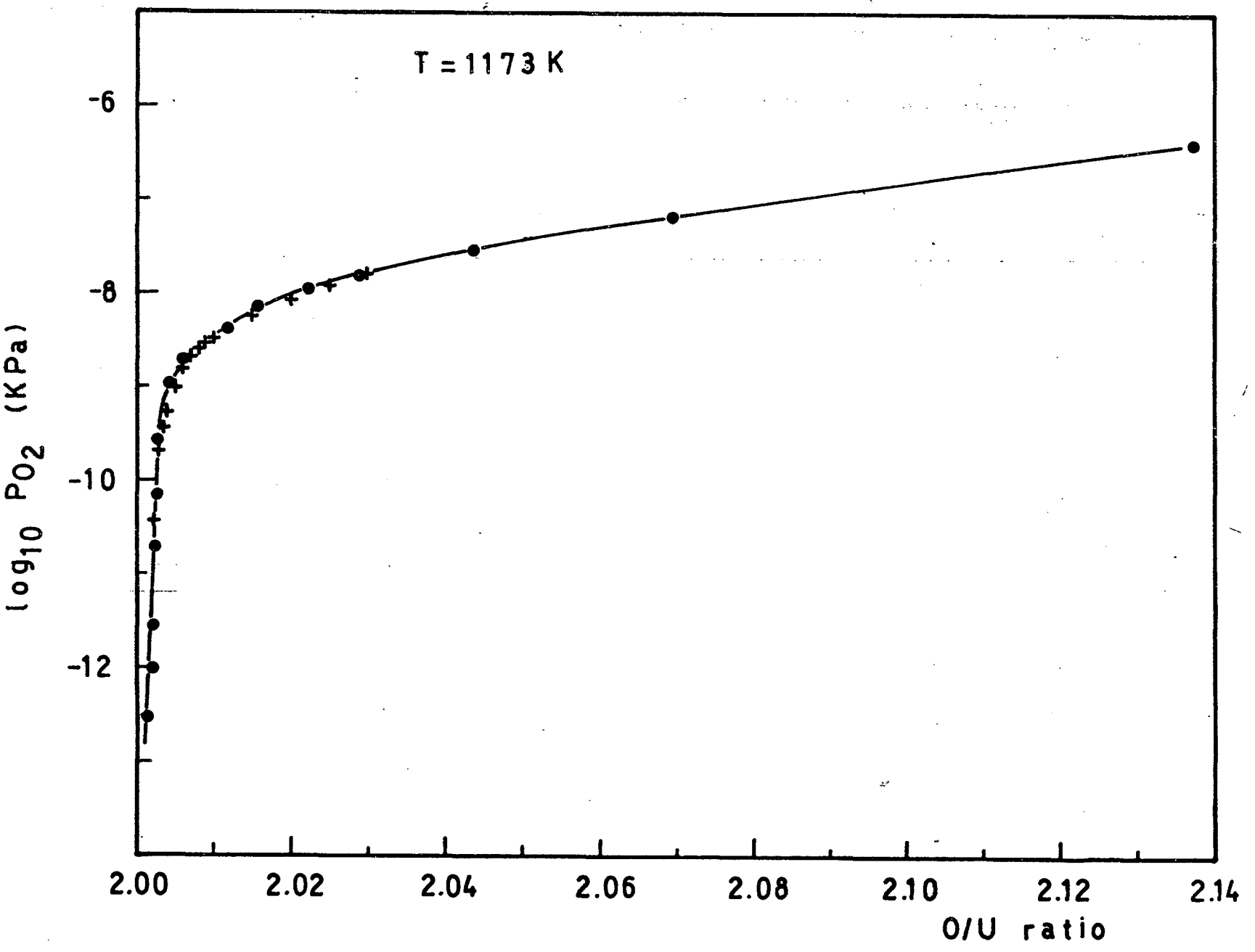
Fig. 1. $\log_{10} P_{O_2}$ as function of O/U ratio in the uranium-oxygen system at 1173 K. + — + Thomas et al. (20). ● — ● this study.

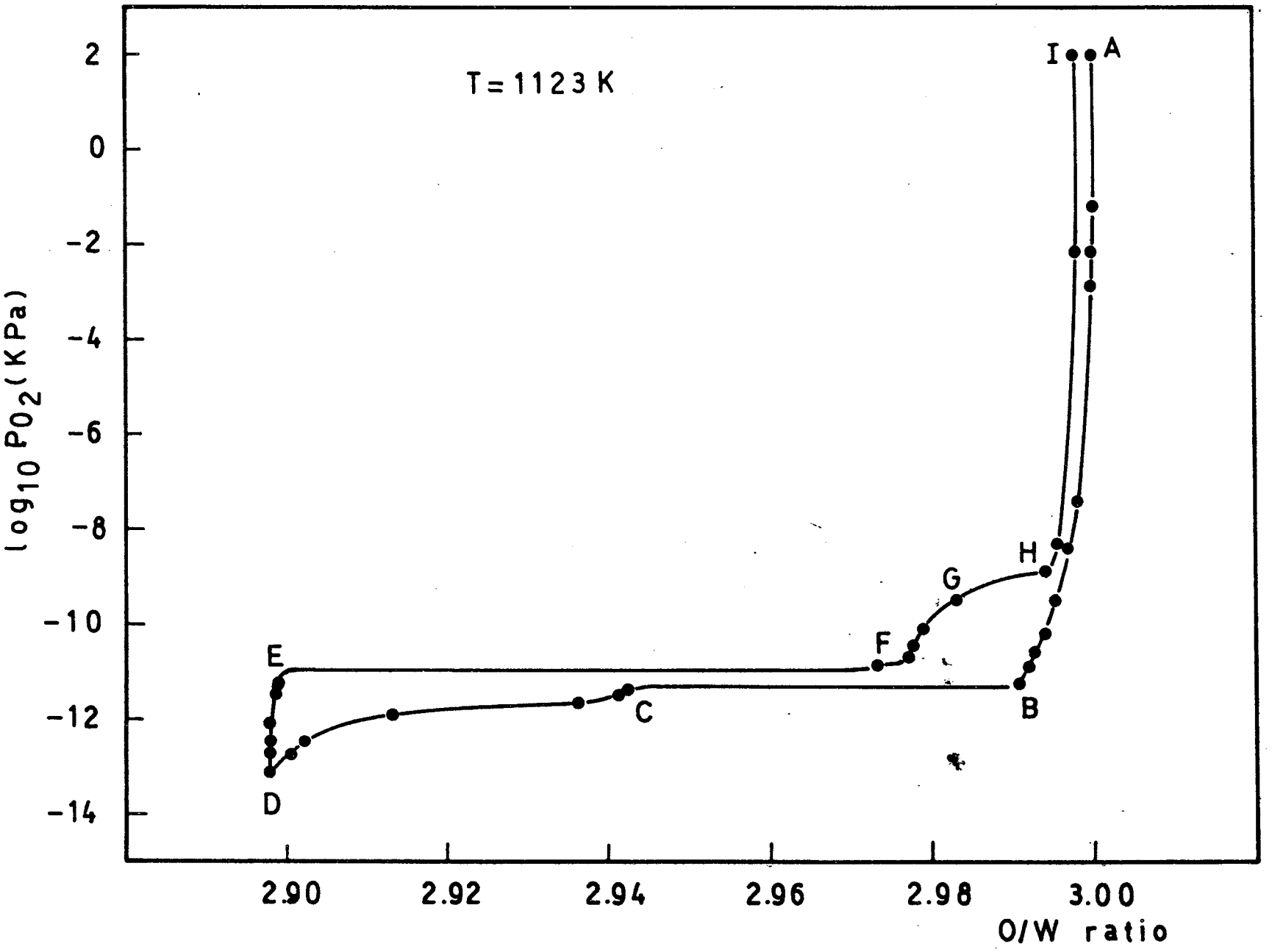
Fig. 2. $\log_{10} P_{O_2}$ as function of O/W ratio in the tungsten-oxygen system, for $2.89 < O/W < 3.00$, at 1123 K.

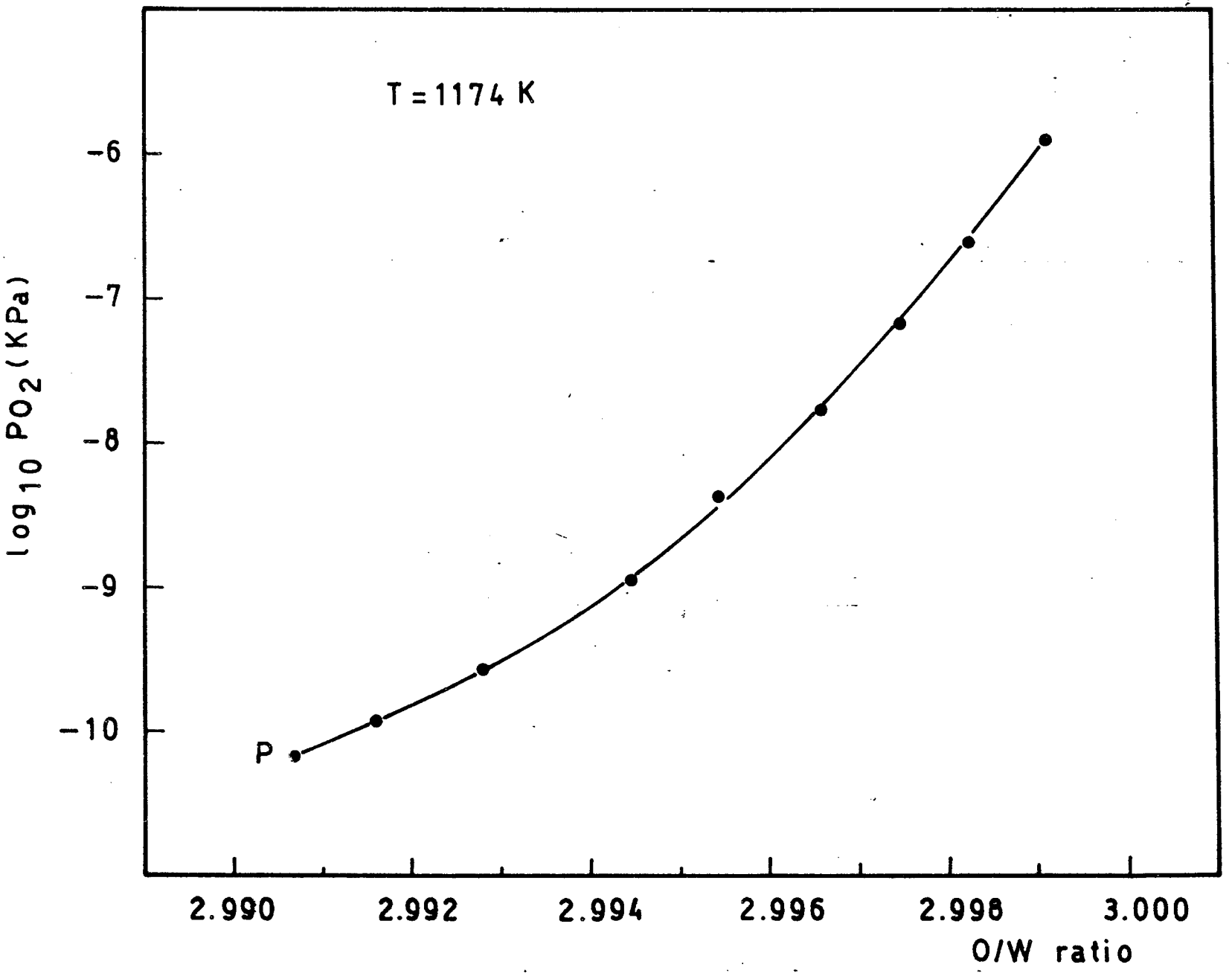
Fig. 3. $\log_{10} P_{O_2}$ versus O/W ratio at 1174 K.

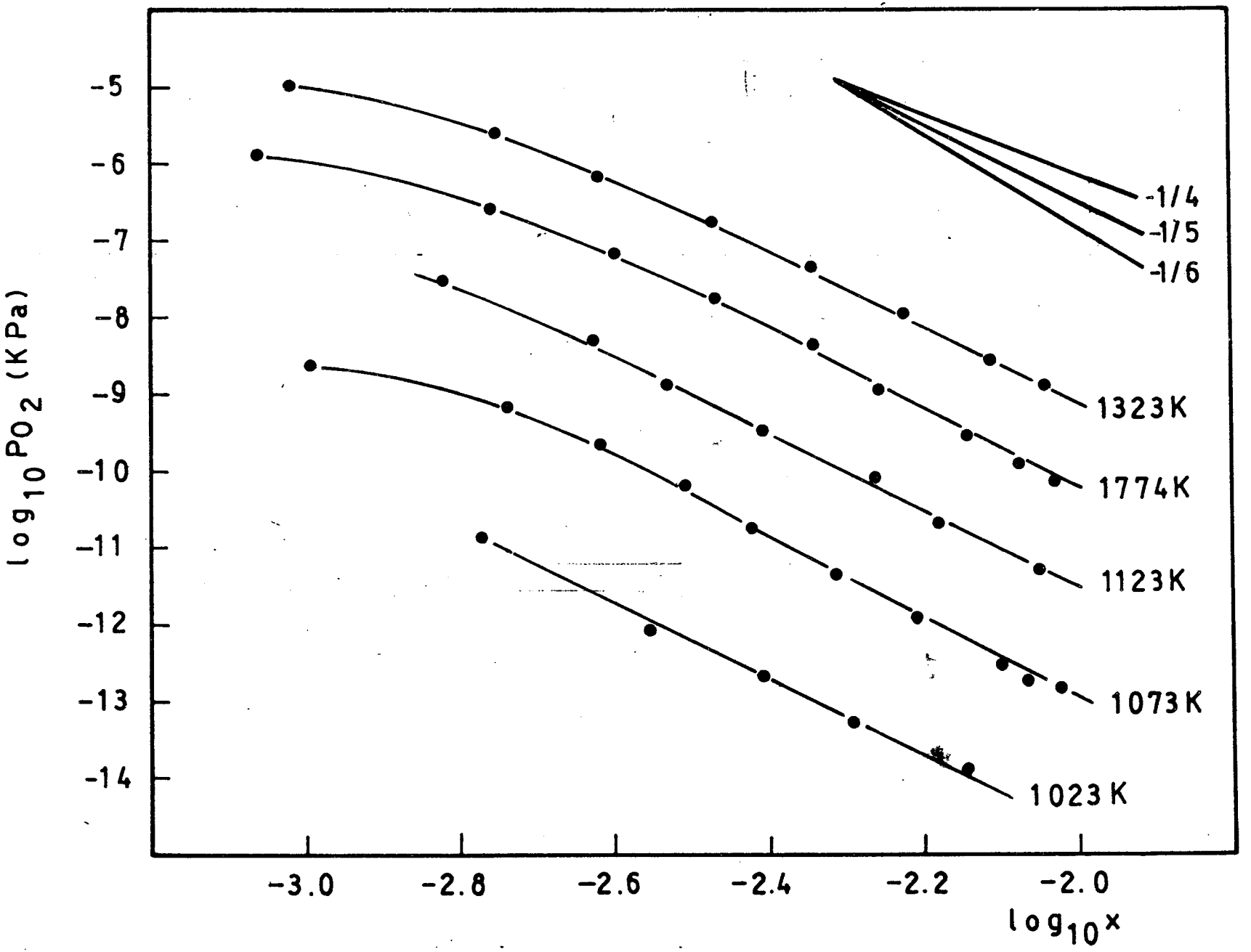
Fig. 4. $\log_{10} P_{O_2}$ as function of $\log_{10} x$, for $2.99 < O/W < 3.00$ at 1023, 1074, 1123, 1174 and 1223 K. In the upper right corner are indicated three straight lines of slopes -1/4, -1/5 and -1/6.

Fig. 5. Oxygen chemical potential for the WO_{3-x} phase as function of temperature and for O/W ratios between 2.9915 and 2.9975.


T = 1173 K
-6
-8
-10
-12
log10 PO2 (KPa)
2.00
2.02
2.04
2.06
2.08
2.10
2.12
2.14
O/U ratio


T = 1123 K
$\log_{10} P_{O_2}$ (KPa)
2
0
-2
-4
-6
-8
-10
-12
-14
2.90
2.92
2.94
2.96
2.98
3.00
O/W ratio
A
B
C
D
E
F
G
H
I


T = 1174 K
-6
-7
-8
-9
-10
log10 PO2 (KPa)
P
2.990
2.992
2.994
2.996
2.998
3.000
O/W ratio


-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
log10PO2 (KPa)
-3.0
-2.8
-2.6
-2.4
-2.2
-2.0
log10x
-1/4
-1/5
-1/6
1323K
1774K
1123K
1073K
1023K