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HIGH-TEMPERATURE THERMODYNAMIC PROPERTIES OF THE THORIUM-OXYGEN SYSTEM

by

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High-Temperature Thermodynamic Properties of the Thorium-Oxygen System*

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ABSTRACT

The thermodynamic properties of the thorium-oxygen system at high-temperatures have been investigated by means of mass effusion, mass spectrometric, and transpiration techniques over compositions ranging from the congruently vaporizing composition to the lower phase boundary composition. A very sharp decrease in oxygen potential occurs when stoichiometric thoria is reduced but slightly from the stoichiometric composition. The small extent of reduction over a wide range of oxygen potentials measured in the temperature range 2400 to 2655 K is a clear illustration of the higher stability of the ThO_{2-x} phase compared with actinide-oxides such as UO_{2-x}, PuO_{2-x}, as well as other metal oxide systems. Estimates of $\Delta\bar{H}_{O_2}$, $\Delta\bar{S}_{O_2}$, and the standard free energy of formation of bivariant ThO_{2-x} compositions have been made. A substantial increase in the total pressure of thorium bearing species occurs when stoichiometric thoria is reduced toward the lower phase boundary. The increase in pressure can be attributed primarily to the increasing contribution of the ThO gaseous species. Total pressures of thorium-bearing species above ThO_{2-x} compositions calculated by means of experimental oxygen potentials and the known or estimated

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free energy of formation values of the gaseous species and condensed phase are in reasonable agreement with experimental values.

Key Words: Thoria, nonstoichiometry, vaporization and stability.

INTRODUCTION

The current interest in the United States of thorium-based fuels as alternative fuels in breeder reactor systems has led us to investigate the high-temperature vaporization behavior of oxygen-deficient thoria.

The thermodynamic properties of the thorium-oxygen system at high temperatures have been determined principally from effusion and mass-spectrometric measurements of vaporization of the virtually stoichiometric dioxide (*1*) and the univariant system, $Th(\ell) + ThO_2(s) + vapor$ (*2*). The most extensive studies of the phase equilibria are reported by Benz (*3*) and clearly show that the dioxide ThO_2 is the only stable oxide in the condensed state. The thorium-oxygen phase diagram as reported by Benz is shown in Fig. 1. The vaporization studies, however, show that both $ThO_2(g)$ and $ThO(g)$ are important molecules in the vapor phase. Rand (*4*) has recently reviewed and critically assessed the physicochemical and thermodynamic properties of thorium compounds and alloys including a detailed analysis of the oxides.

The solid dioxide, thoria, is one of the most stable refractory compounds known and for the most part is well-characterized thermodynamically near the stoichiometric composition (*4*). The phase limits of thoria have not been defined precisely in a chemical sense. The upper phase boundary is generally considered to be ideally stoichiometric ThO_2 because a significantly oxidized or hyperstoichiometric composition would require a valence of thorium exceeding +4 and, therefore, an associated departure from the white color. Benz (*3*) has reviewed the earlier evidence supporting the stoichiometric limit but cites several studies of electrical conductivity and optical properties that suggest some oxygen excess too small to be detected by ordinary chemical methods of analysis. The lower phase boundary as a function of temperature is reported by Benz (*3*) to vary nearly linearly from O/Th = 1.985 ± 0.01 at 1735°C to 1.87 ± 0.04 at 2740°C, the monotectic temperature, and to 1.997 ± 0.01 at the melting point of ThO_2, 3390°C. The rather large uncertainties in composition probably result from the metallographic technique employed. Rauh and Ackermann (*5*) accepted the composition data of Benz for the lower phase boundary (l.p.b.) and calculated the standard free energy of formation of ThO_{2-x}(s) along the l.p.b. with increasing temperature.

The vaporization of thoria in high vacuum produces a congruently vaporizing composition (c.v.c.) that is very close to the stoichiometric composition. Ackermann *et al.*, (*1*) reported O/Th = 1.998 at approximately 2800 K but more recently (*2*) have reported a c.v.c., O/Th = 1.994 ± 0.002 at 2820 K, that was obtained from both oxygen-rich and metal-rich samples. The combustion of crystal-bar thorium metal at 1400°C in air yielded O/Th = 2.000 ± 0.002. Aitken *et al.*, (*6*) have reported a hypostoichiometric composition O/Th = 1.96 produced by heating thoria in "dry" hydrogen at 2600°C.

Very little is known about the interdependence of oxygen potential, total pressure of thorium-bearing species, composition, and temperature in the bivariant region of ThO_{2-x}(s) between the phase limits. The few experimental data of Carniglia *et al.*, (*7*) suggest a dependence of $x \approx p_{O_2}^{-1/6}$, for $0 \leq x \leq 0.003$, $10^{-2} \geq p_{O_2} \geq 10^{-6}$ atm in the temperature range from 1400 to 1900°C. Hence, the experimental results of the present study of thoria are directed toward a more precise and detailed study of the l.p.b., the c.v.c., and intermediate compositions, as well as the corresponding oxygen potentials and total pressures at temperatures above 2000 K.

EXPERIMENTAL

Measurements of the Lower Phase Boundary of Thoria

The lower phase boundary (l.p.b.) of ThO_{2-x} was measured in vacuum in the temperature range from 2005 to 2500 K by the vapor phase equilibration or isopiestic technique (*15*). A mixture of mutually saturated phase, Th(ℓ) contained in a ThO_{2-x}(s) cup, produces an equilibrium vapor at each desired temperature that reduces a physically separate disc or pellet of ThO_2 weighing about one gram. This equilibrated disc, out of contact with the liquid thorium, attains the composition of the lower phase boundary and, after cooling to room temperature, is analyzed by gravimetric combustion analysis in air at 1300 to 1400°C for the O/Th ratio even though disproportionation of the ThO_{2-x} may have occurred. All of the thoria discs were dark gray after the equilibration, but reverted to the original white color after combustion in air. The equilibration times were from 7 to 40 times greater than the minimum time required to transport the amount of ThO(g) necessary to reduce the suspended disc to the l.p.b. The disc must be maintained at a temperature equal to or a few degrees higher than that of the two-phase mixture or else a net condensation of ThO(g) will produce a "too-reduced" composition of the disc which is time dependent. Above 2500 K, a number of experimental difficulties became evident and precluded any reliable determinations of the l.p.b. The physical stability of the Th(ℓ)-ThO_{2-x}(s) mixture began to deteriorate above this temperature, resulting in the rapid penetration of the thoria cup by the liquid metal and the subsequent creep of the liquid metal over the inside surface of the tungsten container.

Measurements of the Congruently Vaporizing Composition

The congruently vaporizing composition (c.v.c.) of thoria was determined over the range of temperature from 2400 to 2820 K by partially vaporizing samples of thoria from a tungsten effusion cell into a vacuum of $\sim 10^{-7}$ torr, following which the compositions of the residues were determined by combustion analysis. The thoria residues were a light to medium gray in appearance, but were not as dark as those obtained in the measurements of the l.p.b. The samples (1.5-2.0 g) reverted to the original white color in the combustion process. The weight gain was determined with a sensitivity of 0.01-0.02 mg. The overall precision of these measurements was somewhat better than that of the l.p.b. measurements because the total vapor pressure is relatively lower and the creep of the metal component was not involved. The

c.v.c. was approached from both the oxidized and reduced condition. In the former case, the sample was immediately heated to the desired temperature for the duration (2-6 hours) of the experiment, whereas in the latter case the sample was initially heated to ∿2800 K to produce the substoichiometric composition at that temperature, and then cooled to the desired temperature (2504 K) in order to approach the c.v.c. from a "too reduced" composition.

Measurements of Oxygen Potentials above Oxygen-Deficient Thoria

The apparatus and general procedure used to measure oxygen potentials and total pressure of thorium-bearing species above bivariant ThO_{2-x} via gas equilibration techniques have been previously described (*8,9*). A small tapered tungsten crucible having a perforated bottom was charged with approximately one gram of sintered granules of stoichiometric thoria and press-fitted into an open-ended tungsten condenser tube. The carrier gas consisted of hydrogen containing varying amounts of moisture, the total pressure of carrier gas was approximately one atmosphere. The oxygen-to-thorium ratio of the residue upon completion of a run was derived from the continuous monitoring of the moisture evolved during reduction of the initially stoichiometric thoria. Oxygen potentials of the H_2-H_2O carrier gas were generally chosen to be more negative than the values estimated for the stoichiometric composition but higher than oxygen potential values estimated for lower phase boundary compositions. However, measurements were also carried out at 2500, 2600, and 2655 K with carrier gas having oxygen potential values slightly higher than the values estimated to establish the stoichiometric composition.

Weight loss measurements of the sample under investigation served as a basis for estimating the total pressure of thorium-bearing species. Previous studies have shown that the agreement between the values of the total pressure of metal-bearing species derived from weight loss measurements and those derived from analysis of the sublimate in the condenser tube is very good (*10*,*11*).

RESULTS AND DISCUSSION

The results of measurements of the lower phase boundary of thoria are shown in Fig. 1 and compared with the metallographic results of Benz (*3*) which are seen to indicate a more reduced state. The results of measurements of the congruently vaporizing composition are also shown in Fig. 2. The previous determination of the c.v.c., O/Th = 1.994 at 2820 K reported by Ackermann and Rauh (*2*) is seen to fall on the curve in Fig. 2; therefore, the frequently cited earlier value (*1*) of 1.998 corresponding to ∿2800 K was obtained on a sample that was apparently not fully reduced.

The extrapolation of the l.p.b. and c.v.c. to higher and lower temperatures can be accomplished by an equation of the form $\log x = A + (B/T)$, where x is the stoichiometric defect in ThO_{2-x}. An equation of this form adequately fits the extensive measurements of the l.p.b. of UO_{2-x} up to 2500 K, some 200° below the monotectic temperature, as pointed out by Winslow (*12*). The results of the present study are shown in Fig. 3 and are seen to fit the linear dependence adequately.

Oxygen potentials corresponding to the univariant system (l.p.b.) $Th(\ell) + ThO_2(s)$ + vapor can be evaluated from the vapor pressure data given by Ackermann and Rauh (*2*) and the critical assessment of thermodynamic data reported by Rand (*4*) for the Th-O system. Ackermann and Rauh report data for partial pressure of ThO(g) in the univariant system:

$$1/2\ Th(s/\ell,\ a \leq 1) + 1/2\ ThO_2(s,\ a \leq 1) = ThO(g) \qquad (1)$$

The combined mass-effusion and mass-spectrometric data correspond to the temperature range from 2020 to 2420 K, but the latter extend below the melting temperature of thorium (2023 K) to as low as 1780 K. At 1800 K the activities of Th(s) and $ThO_2(s)$ can be taken as unity with negligible error because the mutual solubilities of the two condensed phases are indeed small as seen from the phase diagram of Benz (*3*) (Fig. 1) and from the present results for ThO_{2-x} (l.p.b.) seen in Fig. 2.

The equation for the partial pressure of ThO(g) that corresponds to Eqn. (1), $\log p = 7.58 - (28630/T)$ (*2*), combined with the thermodynamic data for stoichiometric thoria and solid and liquid thorium (*4*) yields at 1800 K, $\Delta G_f^\circ(ThO) = -38330$ cal/mol and $\Delta H_f^\circ(ThO,\ 298\ K) = -6980$ cal/mol. Hence, the value of the free energy of formation of ThO(g), $\Delta G_f^\circ(ThO)$, can be generated at any desired temperature from the enthalpy of formation at 298 K and the free energy functions for ThO(g) (*4*). The recalculation of the thermodynamic properties of ThO(g) differs by only ∿500 cal/mol from those reported previously (*2*); the latter were obtained from an equally weighted average of the results of the vaporization data corresponding to Eqn. (1) and those of the isomolecular exchange reaction, $YO(g) + Th(g) = Y(g) + ThO(g)$. A subsequent adjustment by Ackermann and Rauh (*13*) of their previous results (*2*) involved a revision of mass-spectrometric sensitivities and produced values for $\Delta G_f^\circ(ThO)$ that are virtually identical with those obtained from Eqn. (1). The numerical values obtained in the present case are virtually identical to those given by Rand (*4*), who based the third law assessment on the two temperatures, 2080 and 2210 K, at which Ackermann and Rauh (*2*) reported mass-effusion measurements. This fact supports the notion that the activity of Th in the metal-phase and that of ThO_2 in the oxide-phase are closely approximated by the atom fraction, which departs only slightly from unity. Hence, the oxygen potential at the lower phase boundary of the $ThO_{2-x}(s)$ can be evaluated from the equilibrium

$$Th(a_{Th} \approx X_{Th}) + 1/2\ O_2(g) = ThO(g) \qquad (2)$$

for which

$$\Delta\overline{G}_{O_2}(l.p.b.) \doteq 2\Delta G^\circ_f(ThO) + 9.152\ T \log p_{ThO} \qquad (3)$$

In the temperature range from 2200 to 2800 K, Eqn. (3) is closely approximated (within 50 cal/mol) by the linear equation

$$\Delta\overline{G}_{O_2}(l.p.b.) = -295870 + 44.95\ T \qquad (4)$$

By means of a similar calculation scheme and the vaporization data for the congruently vaporization composition (*1*,*2*), one obtains for the equilibrium at the c.v.c.

$$ThO_{2-x}(s,\ a \approx 1) = ThO(g) + (\frac{1-x}{2})\ O_2(g) \qquad (5)$$

the equation for the oxygen potential

$$\Delta\overline{G}_{O_2}(c.v.c.) = -214600 + 37.14\ T \qquad (6)$$

Equations (4) and (6) generate the oxygen potential at each desired temperature, and the corresponding compositions of the l.p.b. and c.v.c. are given by the respective equations shown in Fig. 2. The corresponding pairs of equations can be combined to give the equations

$$\Delta\overline{G}_{O_2}(l.p.b.) = -318450 + 47.27\ T - 4.576\ T \log x \qquad (7)$$

and

$$\Delta\overline{G}_{O_2}(c.v.c.) = -269420 + 46.38\ T - 4.576\ T \log x \qquad (8)$$

Oxygen potentials above bivariant ThO_{2-x} compositions were calculated from the moisture content of the carrier gas by means of the following expression

$$\Delta\overline{G}_{O_2} = 4.576\ T \log p_{O_2} \tag{9}$$

where

$$1/2 \log p_{O_2} = -\frac{12863}{T} + 2.88 - \log \frac{p_{H_2}}{p_{H_2O}} \tag{10}$$

Equation (10) is derivable from well-known thermodynamic data between water vapor and its elements.

The results of oxygen potential measurements above bivariant ThO_{2-x} compositions are shown in Fig. 4 for isotherms in the temperature range from 2400 to 2655 K. The shapes of the isotherms shown in Fig. 4 were obtained from estimated values of the partial molar quantities $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ which were obtained as follows. Figure 5 shows a plot of $\Delta\overline{G}_{O_2}$ versus log x, where x is the stoichiometric defect in ThO_{2-x} for the various isotherms investigated, and for O/Th ratios ranging from c.v.c. to the l.p.b. values. Assuming a linear fit, one obtains from a least-squares analysis of the data, the following expressions

$$2400\ K \quad \Delta\overline{G}_{O_2} = (-258.9 \pm 5.8) - (44.9 \pm 2.2) \log x \tag{11}$$

$$2500\ K \quad \Delta\overline{G}_{O_2} = (-256.0 \pm 2.6) - (48.0 \pm 1.3) \log x \tag{12}$$

$$2600\ K \quad \Delta\overline{G}_{O_2} = (-250.9 \pm 8.8) - (50.3 \pm 4.3) \log x \tag{13}$$

$$2655\ K \quad \Delta\overline{G}_{O_2} = (-251.1 \pm 7.9) - (53.5 \pm 4.0) \log x \tag{14}$$

From these equations, the oxygen partial pressure dependency of x in ThO_{2-x} can be estimated and was found to be approximately proportional to $p_{O_2}^{-1/4}$ over the temperature range from 2400 to 2655 K. From classical defect theory (*14*), this dependency suggests the possiblity that singly charged oxygen vacancies predominate under the conditions of this investigation.

By means of equations (11-14) and the thermodynamic relationships

$$\Delta\overline{S}_{O_2} = \frac{\partial\Delta\overline{G}_{O_2}}{\partial T} \qquad (15)$$

$$\Delta\overline{H}_{O_2} = \Delta\overline{G}_{O_2} + T\Delta\overline{S}_{O_2} \qquad (16)$$

the partial molar enthalpy and partial molar entropy of solution of diatomic oxygen in oxygen-deficient thoria can be estimated for selected compositions. The results are given in Table 1. The sharp changes in $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ suggest the possibility of the occurrence of more than one type of defect for compositions very close to stoichiometry (*15*). It should be emphasized that the accuracy of these values may be somewhat limited by the short temperature range of these measurements (2400-2655 K).

The $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ values given in Table 1 were used to generate the curves in Fig. 4. It is apparent from this study that a very sharp decrease in oxygen potential occurs when thoria is reduced only slightly from the stoichiometric composition. This small extent of reduction over a wide range of oxygen potential occurs when thoria is reduced only slightly from the stoichiometric composition. This small extent of reduction over a wide range of oxygen potential at these temperatures is a clear illustration of the higher stability of the ThO_{2-x} phase than that of UO_{2-x}. For comparison oxygen potentials above UO_{2-x} at 2600 K (*8*) are also included in Fig. 4.

Estimates of the standard free energy of formation of hypostoichiometric bivariant thoria compositions can be made from a knowledge of the relative partial molar free energy values of diatomic oxygen in thoria and the known standard free energy of formation for stoichiometric thoria. The free energy of formation of ThO_{2-x} compositions can be calculated from the Gibbs-Duhem equation in the form

$$\Delta G_f^\circ(ThO_{2-x}, s) = \Delta G_f^\circ(ThO_2, s) - 1/2 \int_{2.00}^{2-x} \Delta\overline{G}_{O_2} \; d(\frac{O}{Th}) \qquad (17)$$

Calculated values of the standard free energy of formation as a function of temperature for the various isotherms investigated are shown in Fig. 6; the temperature coefficients for selected compositions are given in Table 2. It is seen from Fig. 6 that 1) the standard free energy of formation of thoria becomes less negative with increasing oxygen deficiency, and 2) for a given composition, the stability of thoria decreases with increasing temperature. It should be noted that, for a given oxygen-to-metal ratio and temperature, the free energy of formation of thoria is considerably more negative than that of urania (*8*). This again reflects the higher stability of the ThO_{2-x} phase compared with that of UO_{2-x}.

The higher stability of the ThO_{2-x} phase is further illustrated in Table 3 which gives a comparison of nominal $\Delta\bar{H}_{O_2}$ values for various oxide systems.

The results of transpiration measurements of the total pressure of thorium-bearing species above the bivariant Th-O system in the temperature range from 2400 to 2655 K are shown in Fig. 7. The total pressure of thorium-bearing species above virtually stoichiometric thoria seen in Fig. 6 agree within 10% with the effusion results of Ackermann *et al.* (*1*). It is apparent from Fig. 7 that a substantial increase in the total pressure of thorium-bearing species occurs when stoichiometric thoria is reduced toward the lower phase boundary. The increase in pressure can be attributed primarily to the increasing contribution of the ThO gaseous species. It should be noted that the isotherms can be smoothly extrapolated to the vapor pressure values of Ackermann and Rauh (*2*) above the lower phase boundary compositions. For comparison, the total pressure of uranium-bearing species above UO_{2-x} at 2600 K (*9*) is also included in Fig. 7. The striking difference in the curves for UO_{2-x} and ThO_{2-x} is related to the more complex vaporization of

UO_{2-x} involving UO(g), UO_2(g) and UO_3(g) (*9*). Consequently, the congruently vaporizing composition for UO_{2-x} is significantly removed from the stoichiometric composition; however, such is not the case for ThO_{2-x}. From the results given above it follows that uranium-bearing species will predominate in solid solutions of UO_2 and ThO_2 of interest as alternative fuels.

The total pressure of thorium-bearing species above bivariant ThO_{2-x} compositions can be estimated from our experimental oxygen potential values and the known or estimated free energy of formation of the gaseous species and condensed phase. The equations used to generate total pressure values are

$$4.576\ T \log p(\mathrm{ThO,\ g}) = \Delta G_f^\circ(\mathrm{ThO_{2-x},\ s}) - \Delta G_f^\circ(\mathrm{ThO,\ g}) - (\tfrac{1-x}{2})\ \Delta\overline{G}_{O_2} \quad (18)$$

and

$$4.576\ T \log p(\mathrm{ThO_2,\ g}) = \Delta G_f^\circ(\mathrm{ThO_2,\ s}) - \Delta G_f^\circ(\mathrm{ThO_2,\ g}) + (\tfrac{x}{2})\ \Delta\overline{G}_{O_2} \quad (19)$$

where

$$\Delta G_f^\circ(\mathrm{ThO,\ g}) = -16920 - 12.21\ T\ (2200\text{–}2800\ \mathrm{K}) \quad (20)$$

$$\Delta G_f^\circ(\mathrm{ThO_2,\ g}) = -130690 + 6.66\ T\ (2200\text{–}2800\ \mathrm{K}) \quad (21)$$

The results of a typical calculation at 2600 K are shown in Fig. 8. It is seen that the agreement between experimental and calculated total pressure values is reasonable. The significant contribution in the ThO(g) species to the total pressure when stoichiometric ThO_2(s) is reduced towards the lower phase boundary is apparent from the results given in Fig. 8.

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TABLE 1.

Partial Molar Enthalpies and Entropies of Solution of Oxygen in ThO_{2-x}.

O/Th	$-\Delta\overline{H}_{O_2}$ kcal/mol	$-\Delta\overline{S}_{O_2}$ cal/mol °K
1.955	380.6 ± 4.3	75.8 ± 1.7
1.960	381.9 ± 4.0	77.3 ± 1.6
1.965	383.6 ± 3.5	79.1 ± 1.4
1.970	386.1 ± 3.4	81.4 ± 1.3
1.975	388.0 ± 3.4	83.7 ± 1.4
1.980	391.5 ± 3.5	86.9 ± 1.4
1.985	395.0 ± 3.5	90.7 ± 1.4
1.990	400.5 ± 3.9	96.3 ± 1.5
1.995	410.5 ± 6.0	106.0 ± 2.4
1.998	421.5 ± 9.4	118.1 ± 3.7

TABLE 2.

Equations for the Standard Free Energy of Formation of ThO_{2-x}.

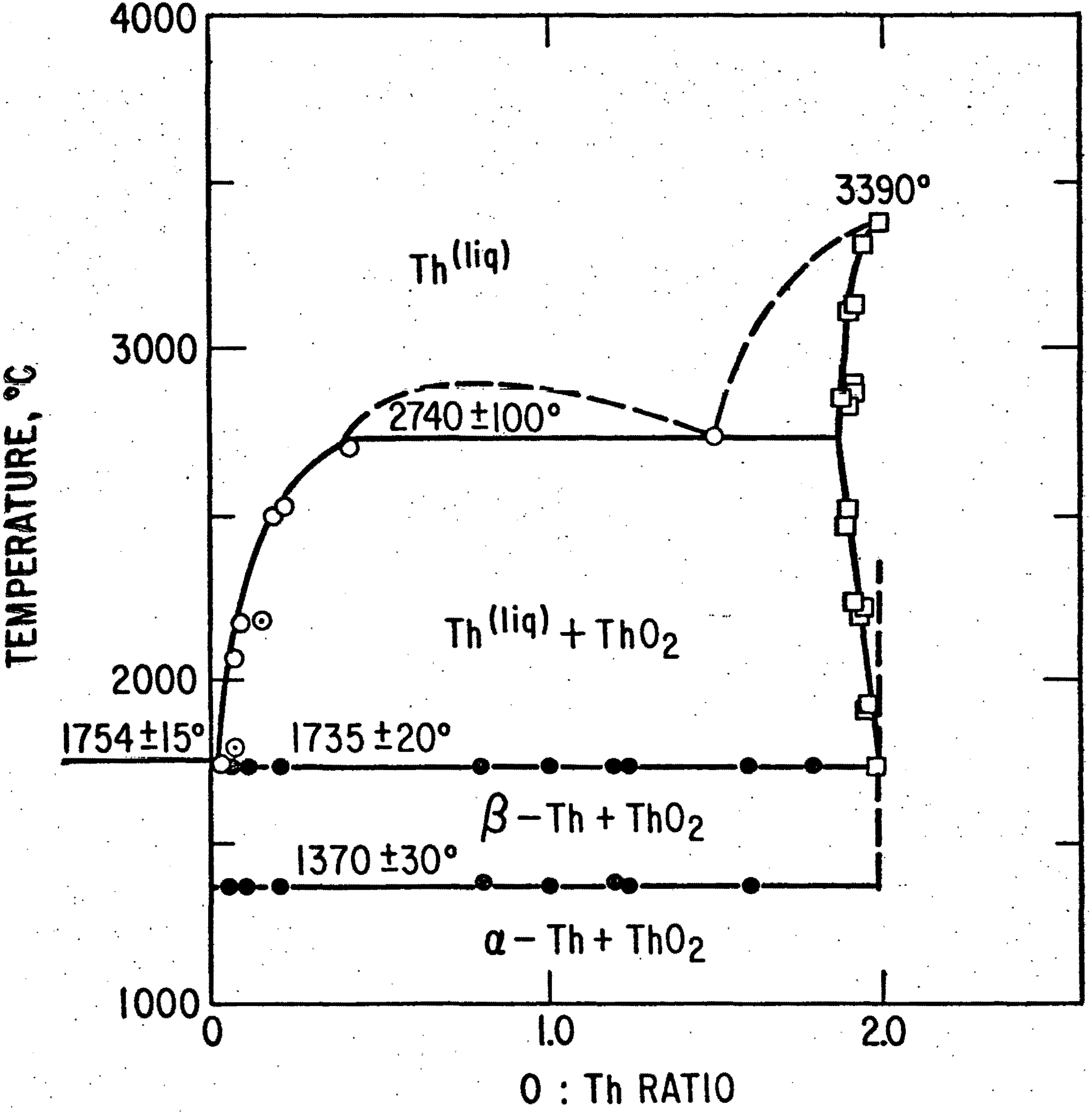
O/Th	$\Delta G_f^\circ = A + BT$, kcal/mol	
	A	B
1.955	-282000	41.0
1.960	-283000	41.2
1.965	-283900	41.4
1.970	-284900	41.6
1.975	-287600	42.4
1.980	-288600	42.6
1.985	-289500	42.9
1.990	-290500	43.1
1.995	-291600	43.4
2.000	-292600	43.7

TABLE 3.

COMPARISON OF PARTIAL MOLAR ENTHALPY OF SOLUTION OF OXYGEN FOR VARIOUS OXIDE SYSTEMS

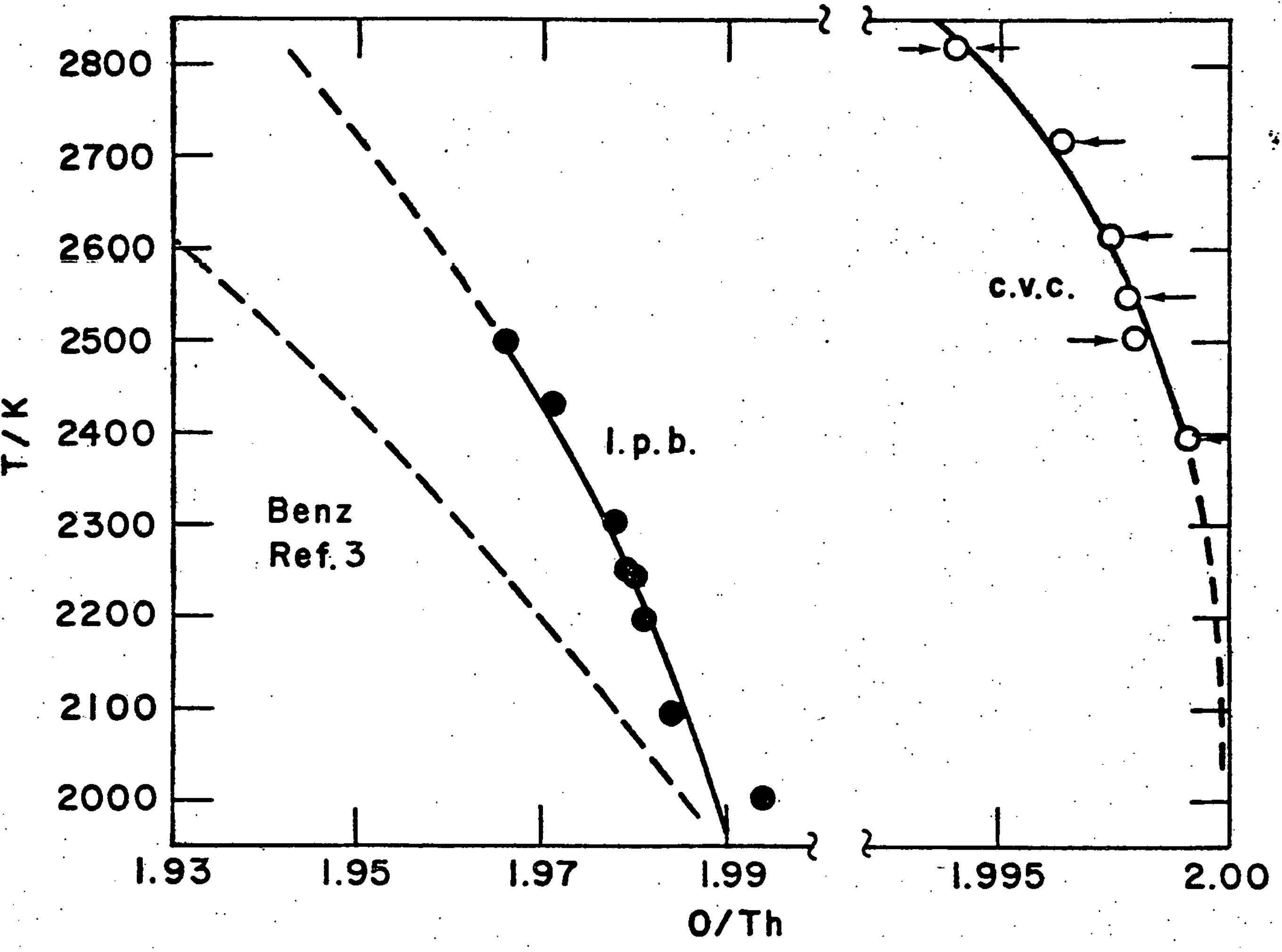
$-\Delta\overline{H}_{O_2}$, kcal/mole

O/M	ThO_{2-x}	UO_{2-x} (8)	PuO_{2-x} (15)	CeO_{2-x} (16)
1.995	411	254	247	228
1.990	391	282	244	224
1.985	384	287	243	221
1.980	381	281	241	216
1.975	379	294	240	214
1.970	379	296	238	211



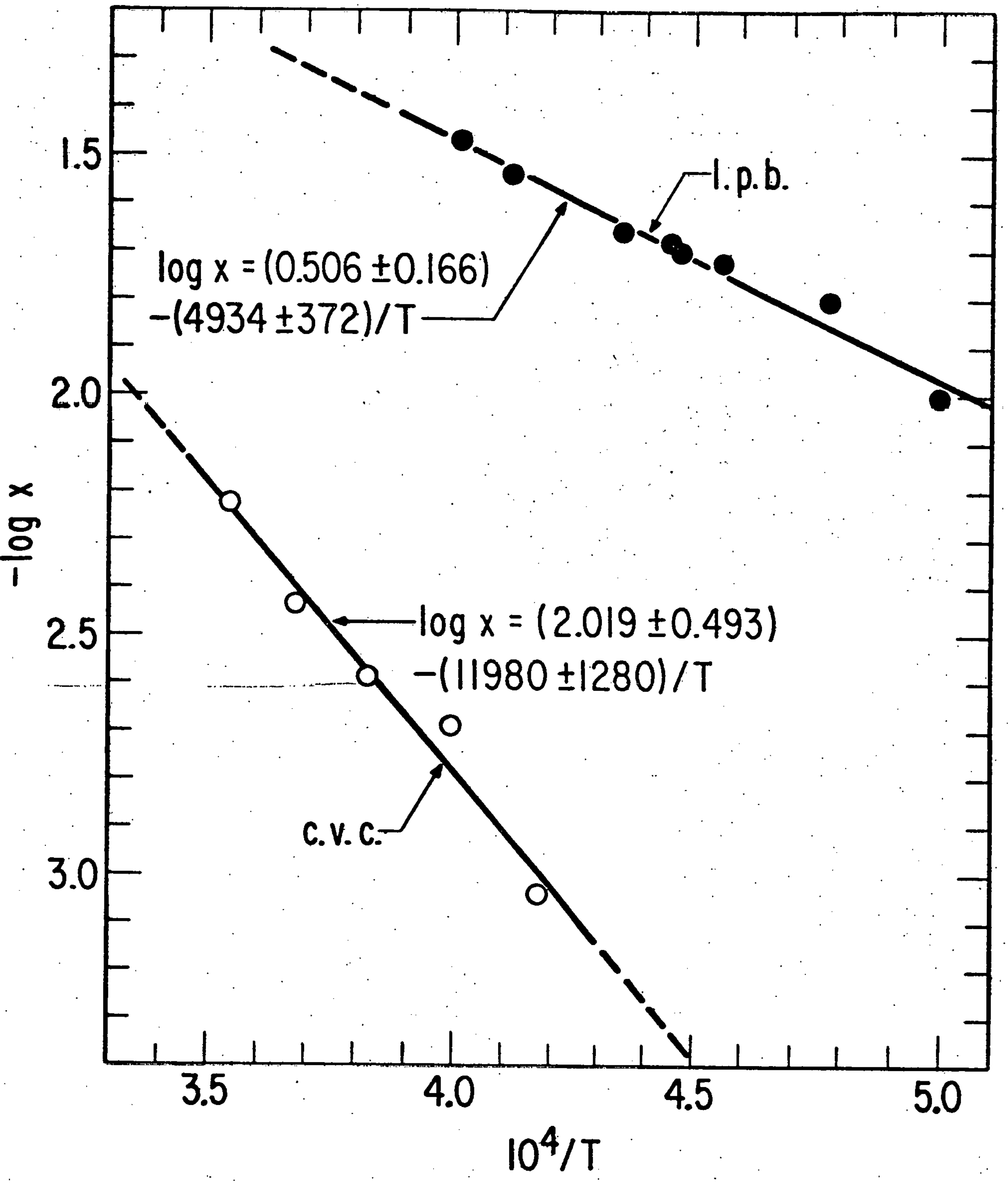
4000
3000
2000
1000
TEMPERATURE, °C
0
1.0
2.0
O : Th RATIO
3390°
Th(liq)
2740 ±100°
Th(liq) + ThO2
1754 ±15°
1735 ±20°
β – Th + ThO2
1370 ±30°
α – Th + ThO2

Fig 1



2800
2700
2600
2500
2400
2300
2200
2100
2000
T/K
1.93
1.95
1.97
1.99
1.995
2.00
O/Th
Benz
Ref. 3
l.p.b.
c.v.c.

Fig 1



1.5
2.0
2.5
3.0
-log x
l.p.b.
log x = (0.506 ±0.166)
-(4934 ±372)/T
log x = (2.019 ±0.493)
-(11980 ±1280)/T
c.v.c.
3.5
4.0
4.5
5.0
$10^4/T$

3

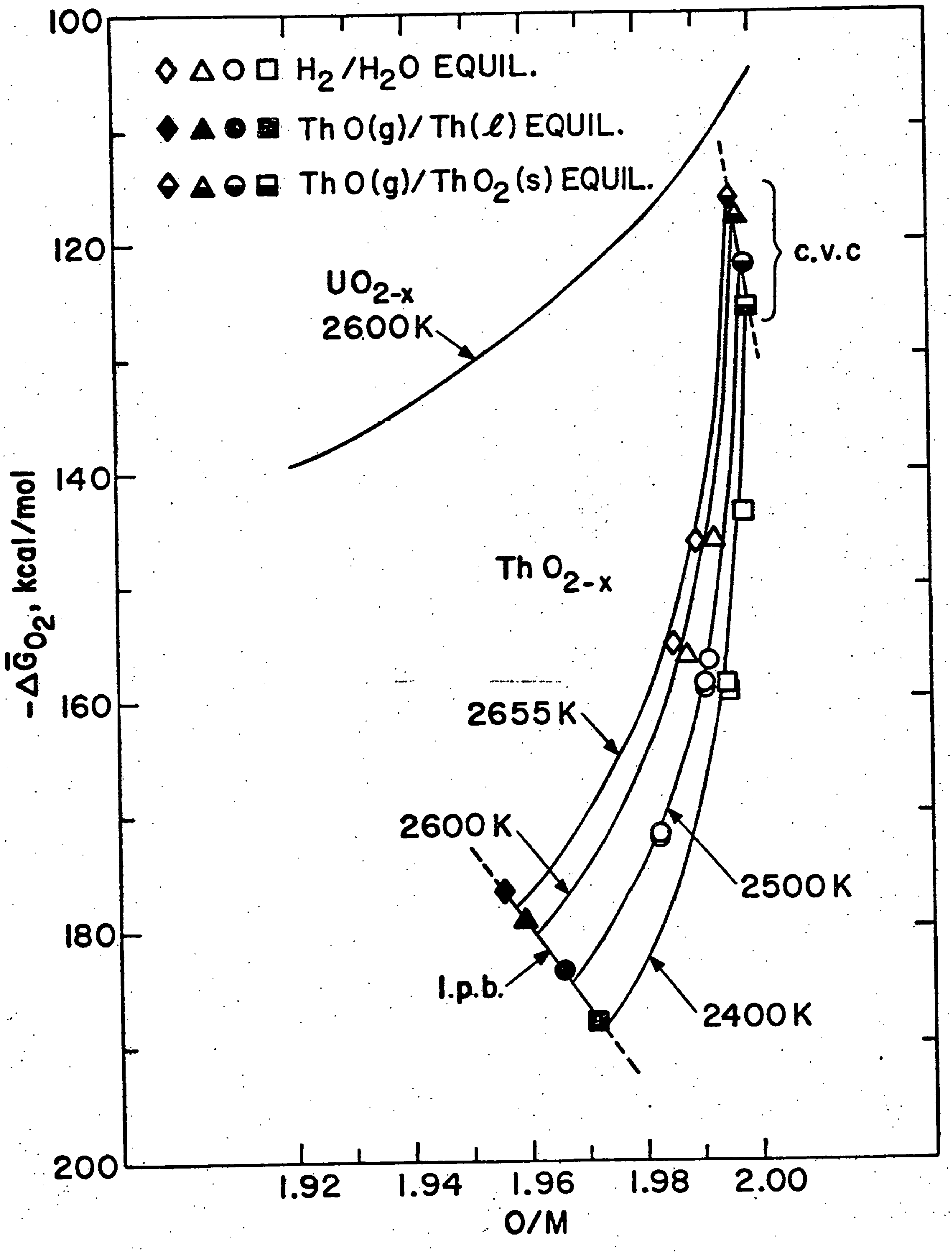
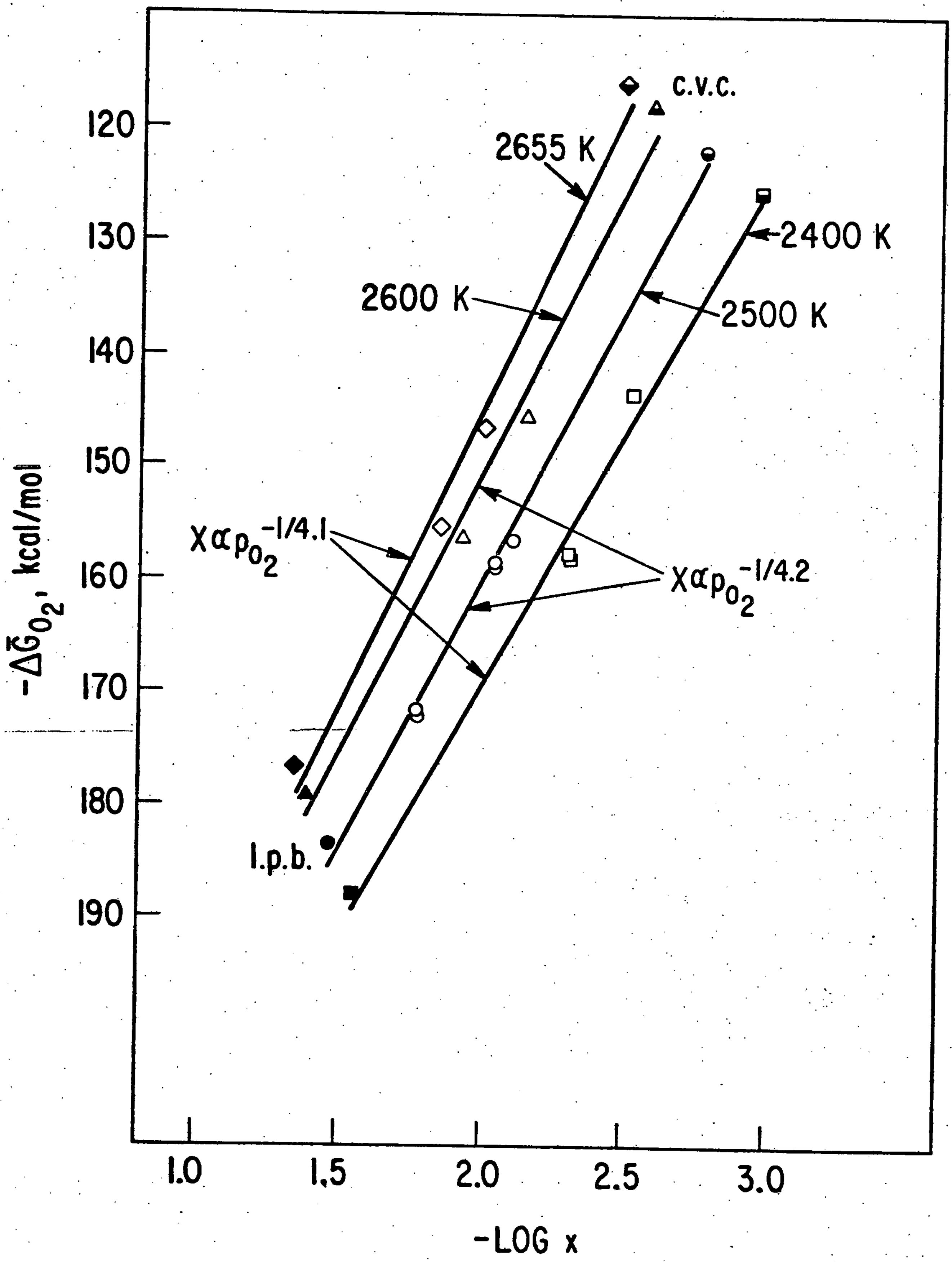

◇ △ ○ □ H_2/H_2O EQUIL.
◆ ▲ ● ■ Th O(g)/ Th(ℓ) EQUIL.
◆ ▲ ◒ ⊟ Th O(g)/ Th O_2(s) EQUIL.
UO_{2-x}
2600 K
c.v.c
Th O_{2-x}
2655 K
2600 K
2500 K
l.p.b.
2400 K
100
120
140
160
180
200
$-\Delta\bar{G}_{O_2}$, kcal/mol
1.92
1.94
1.96
1.98
2.00
O/M

Fig 4


c.v.c.
2655 K
2600 K
2500 K
2400 K
$X \propto p_{O_2}^{-1/4.1}$
$X \propto p_{O_2}^{-1/4.2}$
l.p.b.
120
130
140
150
160
170
180
190
$-\Delta\bar{G}_{O_2}$, kcal/mol
1.0
1.5
2.0
2.5
3.0
-LOG x

5
Fig ~~4~~

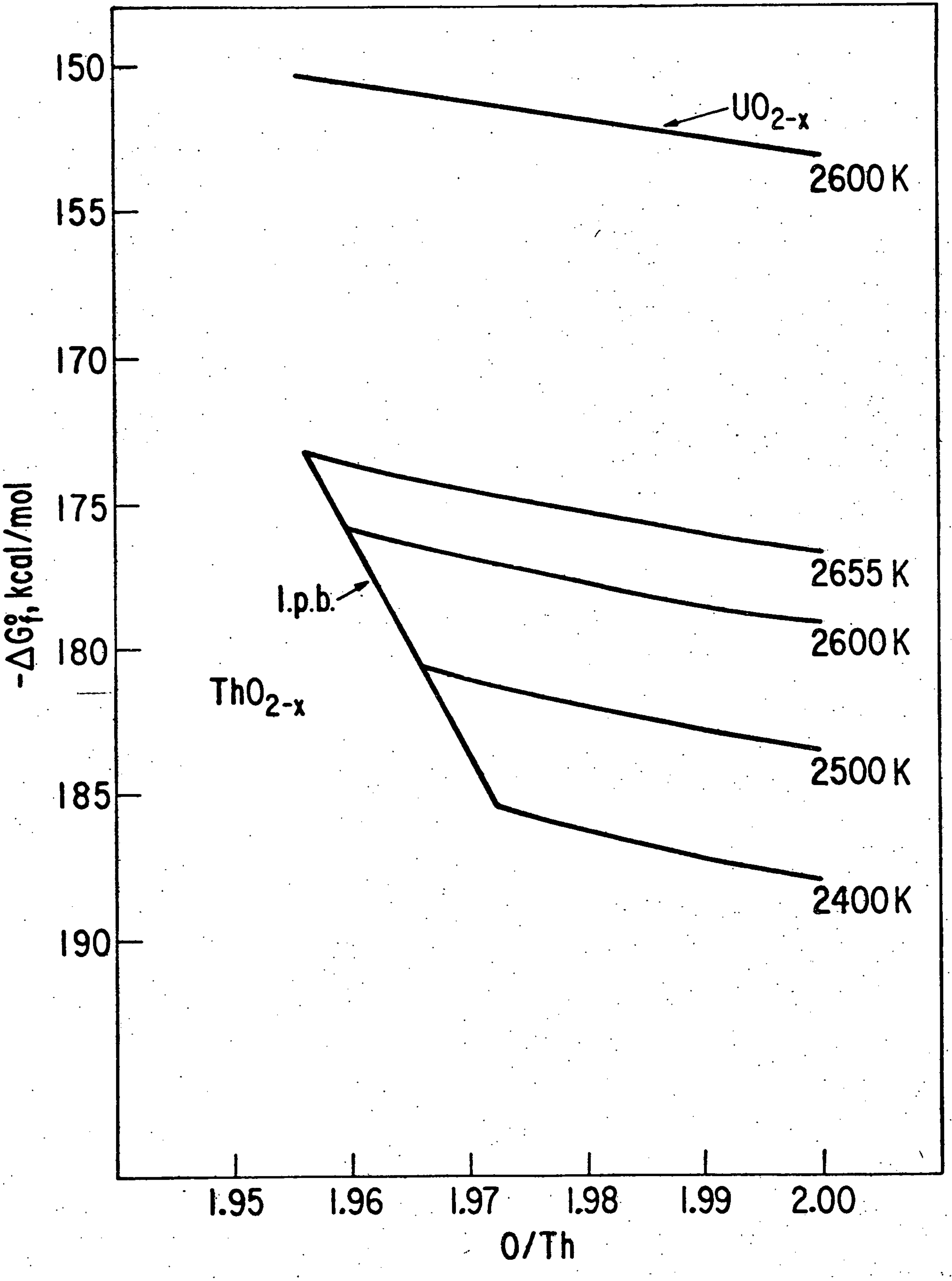
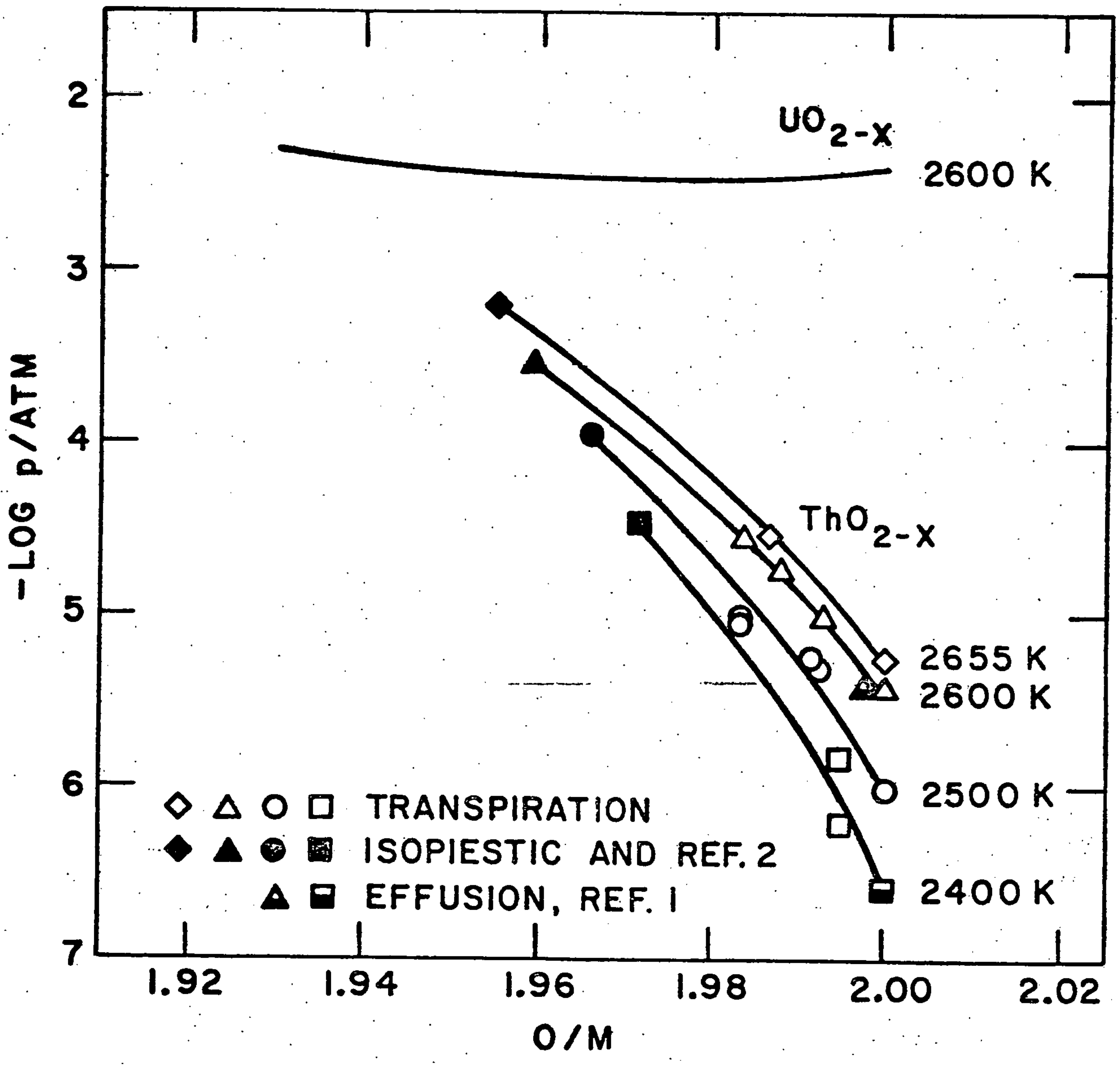

150
155
170
175
180
185
190
$-\Delta G_f^\circ$, kcal/mol
UO_{2-x}
2600 K
2655 K
2600 K
2500 K
2400 K
l.p.b.
ThO_{2-x}
1.95
1.96
1.97
1.98
1.99
2.00
O/Th

Fig 6


UO$_{2-x}$
2600 K
ThO$_{2-x}$
2655 K
2600 K
2500 K
2400 K
◇ △ ○ □ TRANSPIRATION
◆ ▲ ● ■ ISOPIESTIC AND REF. 2
▲ ■ EFFUSION, REF. 1
−LOG p/ATM
2
3
4
5
6
7
1.92
1.94
1.96
1.98
2.00
2.02
O/M

7
Fig

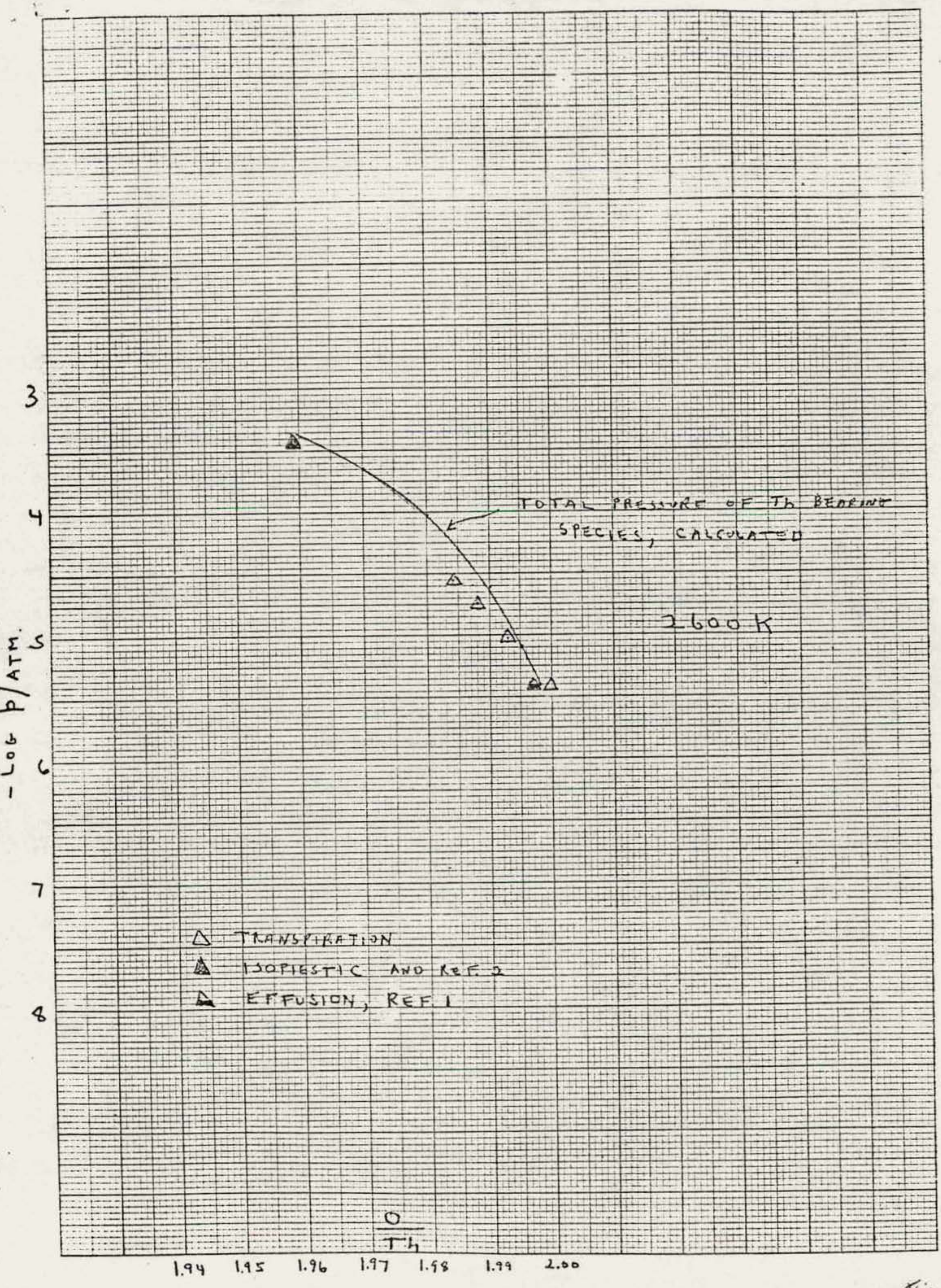

- LOG p/ATM.
3
4
5
6
7
8
TOTAL PRESSURE OF Th BEARING SPECIES, CALCULATED
2600 K
△ TRANSPIRATION
▲ ISOPIESTIC AND REF 2
◭ EFFUSION, REF 1
O/Th
1.94
1.95
1.96
1.97
1.98
1.99
2.00

Fig 8