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INTRINSIC NON-STOICHIOMETRY IN THE LEAD ZIRCONATE-
LEAD TITANATE SYSTEM DETERMINED BY KNUDSEN EFFUSION

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ABSTRACT

The range of the intrinsic non-stoichiometry in lead zirconate-titanate at 1100°C has been established independently by two gravimetric techniques. A modified Knudsen effusion experiment allowed for an interpretation of the vapor pressure data. A single experiment was used to determine the width of any $Pb_{1-x} \square_x (Ti_{1-y} Zr_y) O_{3-x}$ single-phase region, the equilibrium PbO vapor pressure, activity data as a function of both temperature and composition, and the exact location of the stoichiometric composition within the single-phase region. The "vapor phase equilibration," VPE method, was used as a supplemental measurement of the width of most PZT single-phase regions.

Results obtained by the two methods for the extent of non-stoichiometry were in close agreement ($x_{max} = 0.01$ at $y = 1.0$; $x_{min} = 0.016$ at $y = 0.40$; $T = 1100^\circ C$). The Knudsen effusion experiment established that for all compositions studied, the stoichiometric composition, $Pb(Ti_{1-y} Zr_y) O_3$, was coincident with the (liq.+PZT) phase boundary.

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I. INTRODUCTION

Lead zirconate-titanate (PZT) ceramics are of current interest, due in part to the development of several promising image storage and display devices.¹⁻⁴ In these applications, both the electrical and optical properties may be sensitive to the defect structure that is created during the high temperature materials processing.

Recently, it has been shown that a wide variation of stoichiometry (2.5 mol% PbO) is possible in $\text{PbTi}_{.5}\text{Zr}_{.5}\text{O}_3$ at 1100°C.⁵ It would be useful to know the maximum stoichiometric variations that are possible as a result of changes in the processing conditions for any lead zirconate-titanate composition. A method is needed to precisely establish a particular stoichiometry.

The "vapor phase equilibration," (VPE) method, as described in an earlier paper,⁵ affords a unique method of fixing the stoichiometry during processing, while also enabling measurement of the stoichiometric width of most PZT compositions.

However, this measurement technique could not be applied to the solid solution compositions at or quite near pure lead titanate or lead zirconate, because of difficulties encountered in fabricating the required atmosphere crucibles and samples. In addition, a VPE experiment generates no quantitative thermodynamic data. Hence, another approach was taken.

A variation of the standard Knudsen effusion technique allows for an extended interpretation of vapor pressure data. A single experiment may be designed to yield the width of any PZT single-phase region, the equilibrium lead oxide vapor pressure as a function of temperature and

composition, and the exact location of the stoichiometric composition, $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$, within the single-phase region. This is possible because only a single component,^{6,7} PbO , evaporates. The composition of the remaining condensed phase changes uniformly, and can be so constrained to cross the desired phase boundaries at a constant temperature.

In a typical Knudsen experiment, the sample is sealed within a non-reacting cell with a small cylindrical orifice. Ideally, the equilibrium vapor pressure builds up within the cell held at a constant temperature. The orifice area acts as the effective area from which the vapor molecules will escape at the equilibrium rate. This equilibrium escape rate is inferred from the weight-change of the cell, by means of the Knudsen equation:⁸

$$p = (\text{dw}/\text{dt})[2 kT/m]^{1/2}/A_o W \quad (1)$$

where

p = the equilibrium vapor pressure

(dw/dt) = the weight-loss-rate of the cell

T = the orifice temperature in degrees Kelvin

m = the mass of the effusing specie--taken as only the PbO molecule

A_o = the orifice area

W = the Clausing correction factor for the cylindrical orifice

k = Boltzman's constant

In the usual Knudsen effusion method, the vapor pressure is measured above a material of fixed composition. However, because the samples in this study lose PbO by incongruent vaporization, PbO effusion causes the sample composition to change with time.

The experimental variation instituted in this study consisted of initially preparing a well characterized lead zirconate-titanate plus lead oxide sample, continuing the Knudsen effusion experiment until all the lead oxide is exhausted from the cell, and then recording the weight and analyzing the oxide residue. This technique is applicable to any $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ composition.

II. EXPERIMENTAL

A. Sample Preparation

The desired lead zirconate-titanate composition was prepared by carefully mixing the pure oxides in the manner that was previously described⁵ (see Fig. 1). The oxides were mixed with the concentration of lead oxide exceeding that of the required amount (4-16 wt%), to establish the overall sample composition at a known point within the (PZT+PbO) phase field. This powder was calcined in a [PZT+PbO] constant activity multi-phase (CAMP) crucible to allow a brief high temperature soak (3 h, 1100°C) followed by a longer moderate temperature soak (20 h, 850°C) to insure a homogeneous sample. The powder was lightly re-mixed in a plastic mortar and pestle, and screened to remove the particles of less than 400 mesh.

Alternatively, the oxides were combined first in their stoichiometric proportions and calcined at a low temperature in air (840°C, 30 h) to form the $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ compound. Then a precise amount of lead

oxide (4-16 wt%) was added and homogeneously mixed with the PZT.

The overall composition in either case is located on the lead titanate phase diagram¹¹ shown in Fig. 2a near point A.

The powder was poured into the Knudsen cell to yield a low bulk density, which would inhibit sintering at temperature.

B. The Effusion Cell

The Knudsen effusion cells were fabricated from platinum because of its low reactivity with lead oxide. Cylindrical cells were machined from 0.5 in. diameter rod, creating a cavity approximately 0.4 in. by 1.0 in. The cap was machined to the shape shown in Fig. 3 and had an orifice, .013 in. in diameter, 0.15 in. thick. Appropriate corrections were made for the thermal expansion at a mean experimental temperature (1100°C). The Clausing correction for the cylindrical orifice geometry was 0.485.

Temperature measurements were made by a Pt/Pt_{.9}Rh_{.1} thermocouple, spot welded to the cap, as illustrated in Fig. 3. A calibration experiment, with two thermocouples, one welded to the lid, and another welded to the bottom of the cell, indicated the temperature gradient was less than 0.5°C for all temperatures of interest.

The cap and the cell were sealed by heli-arc welding, utilizing a platinum shim. The cap design allowed alternate opening and re-sealing the crucible for a number of experiments.

C. The Thermogravimetric Apparatus

The experimental apparatus is diagrammed in Fig. 4. The balance used was an Ainsworth Recording Balance type RZA-AU-1. The system was

evacuated by means of an oil diffusion pump to pressures in the 10^{-5} to 10^{-4} Torr range.

The furnace was an alumina tube resistance-wound with a Pt.8Rh.2 wire. It was constructed such that the hot zone had a thermal gradient (vertical) of less than 1°C over a 3" zone. A permanently placed thermocouple was calibrated against the spot-welded thermocouple on the cell as shown in Fig. 4.

The cell was suspended by a single thermocouple that was insulated by a high-purity, dense alumina tube. Fine copper coils were employed to mechanically isolate the suspension system while allowing potential measurements from the thermocouple, as shown in Fig. 4.

In most experiments, the thermocouple on the sample cell was used as the controlling thermocouple so that the cell would equilibrate to temperature changes rapidly. Provision was made so that this thermocouple could be connected to a potentiometer, when desired, to obtain accurate temperature measurements.

In some experiments a simpler arrangement was used. The cell was merely suspended by a 0.020 in. diameter Pt._{.9}Rh._{.1} wire, and the temperature was calculated from that of the permanently placed thermocouple.

D. Experimental Procedure

The sample powder was first characterized by X-ray diffraction and chemical analysis for Pb, Ti and Zr content. The Knudsen cell was loosely filled with the powder (approximately 2 grams PZT, 0.40 grams excess PbO), sealed, dried, weighed, fitted with a thermocouple, and installed in the system. This was followed by a bakeout at 600°C for at least 24 h to achieve a stable background pressure in the 10^{-5} to

10^{-4} Torr range. The cell was equilibrated and held successively at several different temperatures (i.e. 750°C, 800°C, 850°C, 900°C) for times long enough to obtain constant weight-loss rates which indicated an equilibrium lead oxide vapor pressure.

Only a small portion of the excess lead oxide in the cell was exhausted during the preliminary weight losses. The sample, still possessing two phases, was then equilibrated at the experimental temperature, 1100°C, while continuously recording the weight loss.

After some time, the loss of PbO significantly altered the sample compositions resulting in the formation of first, single-phase PZT, and then the multi-phase mixture of PZT with titania and/or zirconia. This is illustrated along the 1100°C isotherm drawn on the lead titanate and lead zirconate phase diagrams¹² shown in Figs. 1a and 5, and in the PbO-TiO₂-ZrO₂ isothermal ternary phase diagram¹²⁻¹⁴ reproduced in Fig. 6. When two or more phases are in equilibrium, a constant weight-loss rate is to be expected. Again, the cell was equilibrated at several other temperatures (i.e. 1000°C, 1150°C, 1200°C, 1250°C, etc.), and the constant weight-loss rates that are proportional to the PbO vapor pressures above the multi-phase compositions were recorded.

Finally, the cell was held at 1200°C where a moderate and constant weight loss was expected until the end of the experiment when all PbO had been exhausted from the cell. No further weight loss was observed.

The cell was returned to room temperature, weighed, opened, and the contents weighed, collected, and analyzed. The total observed experimental weight loss should correspond to the amount of lead oxide

initially in the cell.

This experiment could be repeated for any composition within the lead titanate-lead zirconate solid solution system.

E. Vapor Phase Equilibration (VPE) Method

The VPE experiment, described in Ref. 5 for $PbTi_{.5}Zr_{.5}O_3$ was extended to include other compositions of $Pb(Ti_xZr_{1-x})O_3$ where $x = .9, .8, .65, .6, \text{ and } .2$. Porous single-phase PZT samples were equilibrated alternately in high and low CAMP PZT crucibles at $1100^\circ C$ in air. The sample weight changes were monitored continuously by a gravimetric balance. The ultimate weight changes (composition D to composition E shown in Fig. 2b) indicates directly the width of the PZT single phase region. For complete details, see Ref. 5 or 15.

III. RESULTS AND DISCUSSION

The Knudsen effusion experimental data consisted of the effusion generated weight loss of lead oxide from the cell as a function of time at a constant temperature. The Knudsen equation applicable to this system is

$$p(\text{atm}) = 4.675 \times 10^{-7} (dw/dt)[T]^{1/2}/W \quad W = .485$$

W = the Clausing correction for a cylindrical orifice.

No dependence upon the orifice area was found when an orifice diameter of 18 mils (doubling the orifice area) was used for PbO and $PbTiO_3$ experiments.

When during the course of the experiment the lead oxide effusion caused the sample composition to cross into the PZT single phase region, the weight-loss rate observed became non-linear and alower, reflecting the reduced lead oxide activity in the sample as it becomes more

deficient with respect to PbO. When the continuous effusion of lead oxide caused the appearance of a new second phase (i.e. titania as in Fig. 1a, the weight-loss rate, and therefore the vapor pressure, will again become constant. Thus, the amount of lead oxide lost during the non-linear portion of the weight-loss data will correspond to the exact width of the PZT single-phase region with respect to PbO at that temperature, or the degree of non-stoichiometry of the compound.

This non-linear region is measurable for all lead zirconate-titanate compositions, is quite reproducible, and is independent of the amount and particle size distribution of the sample powder. However, screening techniques were always used to remove the smallest particles from the distribution.

Figure 7 summarizes an entire experiment. The actual results are summarized in Table I. The variation found in the width of the PZT single-phase regions is illustrated graphically in Fig. 8 in mol% PbO lost from the sample, mol% lead vacancies in the sample, and in mole fraction of PbO. This relation is drawn to scale on the ternary phase diagram in Fig. 6, the PbTiO_3 phase diagram in Fig. 2a, and the lead zirconate phase diagram in Fig. 5. It is seen that both the terminal compositions, lead titanate and lead zirconate, possess the widest ranges of non-stoichiometry in the system.

X-ray diffraction techniques were used to identify the low temperature PZT phases as a function of non-stoichiometry. Gerson¹⁸ has reported the low temperature phases for essentially stoichiometric PZT compositions. The results do not appear to be constant across the single-phase region. Stoichiometric $\text{Pb}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_3$ is a tetragonally distorted

perovskite, while the non-stoichiometric material produces diffraction lines corresponding to a mixture of rhombohedral and tetragonal phases. This indicates that the non-stoichiometric material is located on the phase boundary. A sketch, based on the analysis of several other compositions, is provided in Fig. 9. No attempt was made to characterize the Curie temperature variation across the single-phase regions.

Assuming the rate of weight loss to be proportional to the vapor pressure of PbO within the cell at all times, tangents constructed to the weight-loss curve allow calculation of the lead oxide vapor pressure or activity as a function of composition. The non-linear portion of one experiment is shown in Fig. 10.

The data allowed the graphical integration of the Gibbs-Duhem equation^{19,20} which yield the corresponding activity of titania or zirconia and consequently the free energy of mixing as a function of composition through the PZT single-phase region. This calculated free energy of mixing is found to have a minimum within the single-phase region implying that the stoichiometric composition is not the most stable perovskite. The details of the analysis and the computer assisted calculation are presented in Ref. 15. This analysis was applied to both lead titanate and lead zirconate. The experimental results for the activity as a function of composition are shown in Fig. 11 for PbTiO_3 and in Fig. 12 for PbZrO_3 . The results for the free energy of mixings dependence on composition is given for both materials in Fig. 13.

Each experiment generated lead oxide vapor pressure data for the multi-phase regions that bound the non-stoichiometric compound. The results that were obtained compare favorably with those reported by

Hardtl and Rau²¹ for the (PZT+Z) phase field.

Pure lead oxide was used as a calibrating material since it has been extensively studied and is the only vapor species of consequence in the system.^{5,6} Vapor pressure data were obtained for pure lead oxide that are in excellent agreement with the thermochemical data as tabulated by Kubaschewski et al.²² and JANF tables,²³ and in fair agreement with the lead oxide standard used by Hardtl and Rau.²¹ The results are shown in Fig. 14.

The lead oxide vapor pressures obtained for the PZT composition in equilibrium with either the lead rich liquid phase or the oxide solid phase, are presented in Figs. 15 and 16. The vapor pressure expressions, the enthalpy, entropy, and the standard deviations are given in Table II. (The data points were least squares fitted to the linear form, $\ln p = A(1/T)+B$.)

Because PbO is the only significant vapor species in the PbO-TiO₂-ZrO₂ system, it is expected that a second law analysis of the Knudsen effusion vapor pressure data should yield equivalent values for the entropies of vaporization. This is observed (Table II) for PbO, PbTiO₃+TiO₂, and PbZrO₃+ZrO₂.

Entropy and enthalpy are defined assuming a composition that is invariant with temperature. Entropy correlation cannot be expected for PbTiO₃+liquid or PbZrO₃+liquid, as the lead rich liquid compositions change appreciably with temperature (see Figs. 1a and 5). Consequently, constants reported in Table II for these cases do not correspond to true entropies or enthalpies.

The composition of the vapor is assumed to be essentially monomer. Small amounts of dimer and trimer lead oxide in the vapor above pure condensed lead oxide⁵ introduce small errors, but these are not believed to be important.

A plot of the lead oxide activity of PZT in equilibrium with a lead rich liquid as a function of temperature (Fig. 17) and the $Pb(Ti_xZr_{1-x})O_3$ compositions is shown in Fig. 18. While the results for PZT in equilibrium with titania and/or zirconia are in good agreement with those reported by Hardtl and Rau,²¹ Atkin and Fulrath's²⁴ approximation of PbO activity for PZT plus lead rich liquid compositions which assumed the applicability of Raoult's law for the liquid based on the phase equilibria information reported by Fushimi and Ikeda,¹² is found to be in error. The actual activity coefficients as calculated from the present experimental data, deviate substantially from Raoult's law and are plotted as a function of composition in Fig. 19.

IV. CONCLUSIONS

The range of non-stoichiometry in lead zirconate-titanate at 1100°C has been established by two different gravimetric techniques. A modified Knudsen effusion experiment was utilized to indicate:

1. The width of the $Pb_{1-x} \square_x (Ti_yZr_{1-y})O_{3-x} \phi_x$ single phase region at 1100°C [$x_{max} = 0.01$ at $y=1.0$; $x_{min} = 0.016$ at $y=0.40$].

2. The variation of the PbO vapor pressure and activity with temperature for pure PbO, PZT+PbO, and PZT+Z+T compositions (equivalent values for the entropy of vaporization of PbO and PZT+Z+T [$\Delta S = 34.5 \pm 1.4$ eu] were obtained).

3. The continuous variation of PbO vapor pressure and activity with composition across the PZT single-phase region at 1100°C.

4. The location of the stoichiometric compound relative to the determined phase boundaries were found to coincide with the liquid and solid phase boundary.

Lead zirconate-titanate can be treated as a three-component system, with only lead monoxide molecules as the major vapor species.

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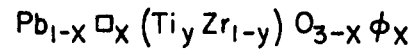
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TABLE HEADINGS

Table I. Tabulated results of the "Vapor phase equilibration (VPE)" experiment and the Knudsen Effusion (KE) experiment defining the extent of non-stoichiometry or width of the PZT single-phase region.

Table II. Tabulation of linear least squares fit to the Knudsen Effusion experiments.



y	ΔW SINGLE-PHASE WIDTH			SAMPLE COMPOSITION (BOUNDARY)					EXPERIMENTAL METHOD	
	WT. %	"MOL. % PbO"	x	MOL. % PbO	MOL. % □, φ	MOL. % TiO ₂	MOL. % ZrO ₂	MOL. FRACTION PbO	V.P.E.	K.E.
1.0	7.36	10.0±1.0	0.100	45.0	5.0	50.0	0	0.474		X
0.9	4.01	5.5±0.5	0.055	47.25	2.75	45.0	5.0	0.486	X	X
0.8	3.1	4.2±0.5	0.042	47.9	2.1	40.0	10	0.490	X	X
0.65	1.89	2.7±0.3	0.027	48.65	1.35	32.5	17.5	0.493	X	X
0.5	1.72	2.48±0.3	0.025	48.75	1.25	25.0	25.0	0.494	X	X
0.4	1.08	1.6±0.2	0.016	49.2	0.8	20.0	30.0	0.495	X	X
0.2	1.98	3.0±0.5	0.030	48.5	1.5	10.0	40.0	0.4925	X	X
0	6.1	9.5±1.0	0.095	45.475	4.525	0	50.0	0.475		X

FORMULAE USED

$$(1) \text{ "MOL. \% PbO" } \equiv \frac{\text{NO. MOLES PbO LOST}}{\text{NO. MOLES PbO IN SAMPLE}} (100) = \frac{(\delta W)(\text{MW-PZT})}{223.19 (W_s)} (100)$$

δW = SAMPLE WT. LOSS

$$(2) \text{ "WT. \% PbO" } \equiv \frac{(\text{GRAMS PbO LOST})}{(\text{GRAMS PbO IN SAMPLE})} (100) = \frac{(\delta W) (100)}{[(W_s)/(\text{MW-PZT})] (223.19)}$$

W_s = INITIAL SAMPLE WT.

MW-PZT = MOLECULAR WT.

$$\text{ "WT. \% PbO" } = \text{ "MOL. \% PbO" }$$

$$(3) \text{ WT. \% } \equiv \frac{\text{GRAMS LOST}}{\text{SAMPLE WT.}} \times 100 = \frac{\delta W}{W_s} \times 100$$

$$(4) \text{ MOL. \% PbO } = \frac{(1-x)}{2} (100) \quad \text{MOL. \% TiO}_2 = \frac{y}{2} (100)$$

$$\text{MOL. \% } \square, \phi = \frac{x}{2} (100) \quad \text{MOL. \% ZrO} = \frac{(1-y)}{2} (100)$$

$$(5) \text{ MOLE FRACTION PbO } = \frac{1-x}{(1-x)+1} = \frac{1-x}{2-x}$$

XBL726-6457

KNUDSEN SAMPLE COMPOSITION	LINEAR LEAST SQUARES FIT		SECOND LAW ANALYSIS	
	A	B	ENTHALPY	ENTROPY
PbO	-2.916×10^4 $\sigma = 9.07 \times 10^2$	17.405 $\sigma = 0.788$	-5.795×10^4 $\sigma = 1.8 \times 10^3$	34.59 $\sigma = 1.56$
PbZrO ₃ + PbO(l)	-2.64×10^4 $\sigma = 4.47 \times 10^2$	14.70 $\sigma = 0.359$	-5.255×10^4 $\sigma = 8.89 \times 10^2$	29.21 $\sigma = 0.714$
PbTiO ₃ + PbO(l)	-2.25×10^4 $\sigma = 5.13 \times 10^2$	10.75 $\sigma = 0.424$	-4.471×10^4 $\sigma = 1.02 \times 10^3$	21.36 $\sigma = 0.843$
PbZrO ₃ + ZrO ₂ ss	-31.86×10^4 $\sigma = 9.75 \times 10^2$	16.75 $\sigma = 0.734$	-6.33×10^4 $\sigma = 1.94 \times 10^3$	33.29 $\sigma = 1.45$
PbTiO ₃ + TiO ₂ ss	-3.64×10^4 $\sigma = 9.18 \times 10^2$	17.89 $\sigma = 0.648$	-7.23×10^4 $\sigma = 1.82 \times 10^3$	35.55 $\sigma = 1.289$

LEAST SQUARES FIT TO KNUDSEN CELL DATA OF FORM:

$$\ln P_{\text{PbO}} = A (1/T) + B \quad A = \Delta H/R \quad B = \Delta S/R$$

σ = STANDARD DEVIATION

XBL 726 6456

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FIGURE CAPTIONS.

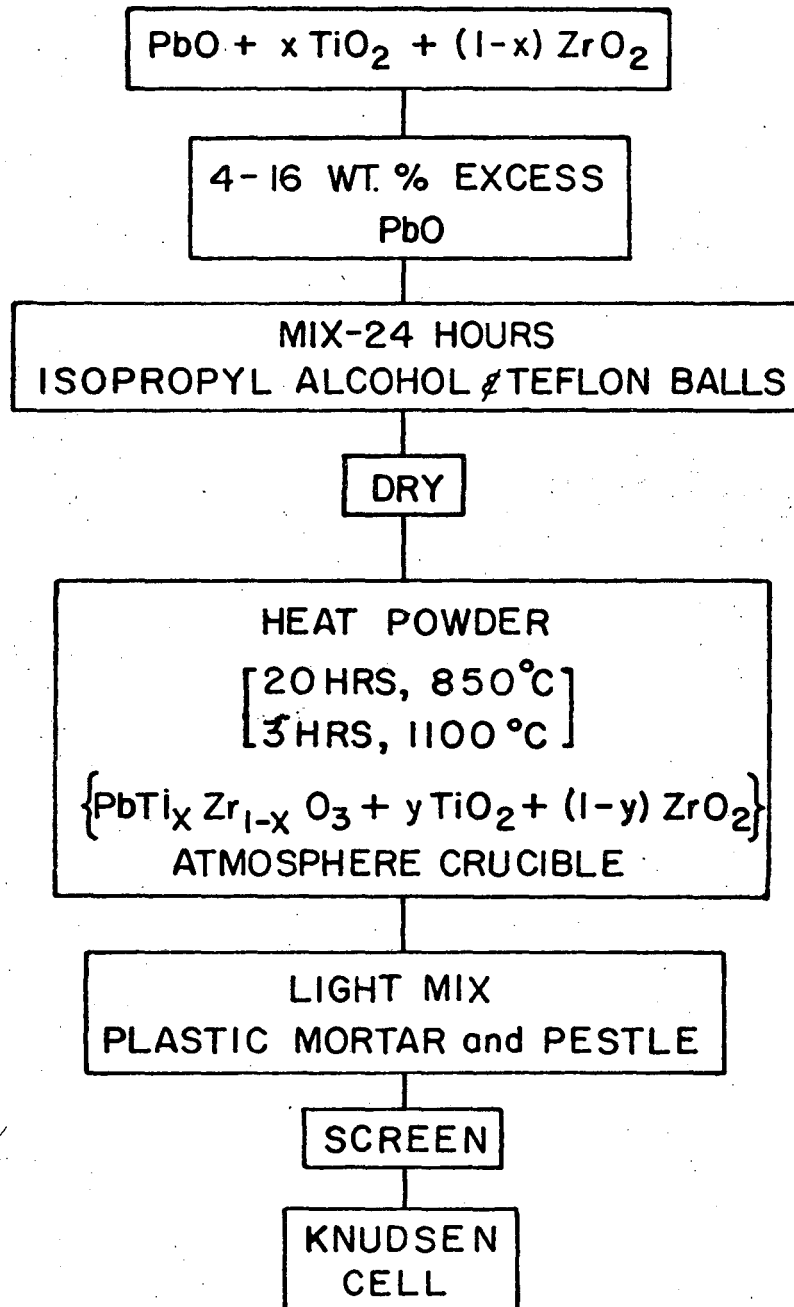
- Fig. 1. Processing flow diagram for the Knudsen sample.
- Fig. 2. (a) Proposed PbO-TiO_2 phase diagram after Moon,¹¹ and assuming a lead titanate region of non-stoichiometry.
(b) Activity of PbO vs. mole fraction PbO at constant temperature (1100°C) for the lead titanate binary.
Points A and B designate the constant PbO atmospheres provided by the CAMP crucibles of these compositions; point C locates the composition and activity of the nearly stoichiometric single-phase compound, whereas D and E indicate the single-phase boundaries.
- Fig. 3. Sectioned view of the Knudsen Effusion cell. Platinum shims are employed to allow sufficient heli-arc welding for a seal. The cell is suspended by a $\text{Pt/Pt}_{.9}\text{Rh}_1$ thermocouple, with the temperature measuring junction created by the $\text{Pt}_{.9}\text{Rh}_{.1}/\text{Pt}$ cell junction.
- Fig. 4. The experimental apparatus used in the Knudsen Effusion experiments. The continuously recording microbalance with automatic weight-change mechanism is an Ainsworth type RZA-AU-1. Thin copper coils from the sample suspension thermocouple to a terminal strip that may be reached by a vacuum feedthrough, serve to create mechanical isolation while providing electrical conduction.
- Fig. 5. The PbO-ZrO_2 phase diagram after Fushimi¹² and including the experimentally measured lead zirconate non-stoichiometry at 1100°C .

- Fig. 6. The PbO-TiO_2 isothermal ternary phase diagram at 1100°C . The tie-lines in the PZT + LIQUID region were determined by Fushimi and Ikeda.^{12,14} The phases present in the lower portion of the diagram were determined by Webster et al.¹³ The variation in the width of the $\text{PbTi}_x\text{Zr}_{1-x}\text{O}_3$ single phase region is drawn to scale.
- Fig. 7. Knudsen cell weight loss vs time during a typical experiment. Equilibration at successive temperatures on both sides of the single-phase region allows efficient collection of vapor pressure data. ΔW , corresponding to the weight-loss from B to C on the activity diagram, measures the width of the PZT single phase region.
- Fig. 8. Variation of non-stoichiometry in the lead titanate-lead zirconate solid solution system.
- Fig. 9. Low temperature phase system of $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ modified to include the effect of non-stoichiometry. Tetragonal $\text{Pb}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_3$ becomes tetragonal + rhombohedral $\text{Pb}_{.975}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_{2.975}$; tetragonal $\text{Pb}(\text{Ti}_{.65}\text{Zr}_{.35})\text{O}_3$ becomes tetragonal $\text{Pb}_{.973}(\text{Ti}_{.65}\text{Zr}_{.35})\text{O}_{2.973}$.
- Fig. 10. Expanded non-linear portion of the Knudsen cell weight loss vs time data (single-phase region) allowing calculation of the lead oxide activity variation with composition through the single-phase region.
- Fig. 11. Lead oxide and titania activity as a function of composition in the lead titanate single-phase region as determined from analysis of the Knudsen effusion data and a graphical

integration of the Gibbs-Duhem equation.

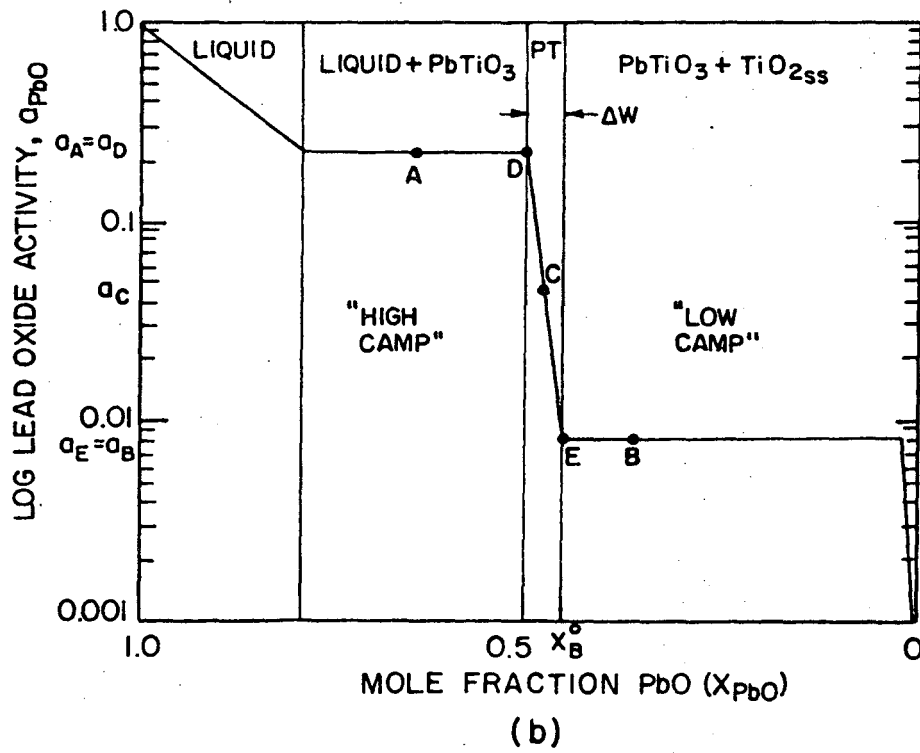
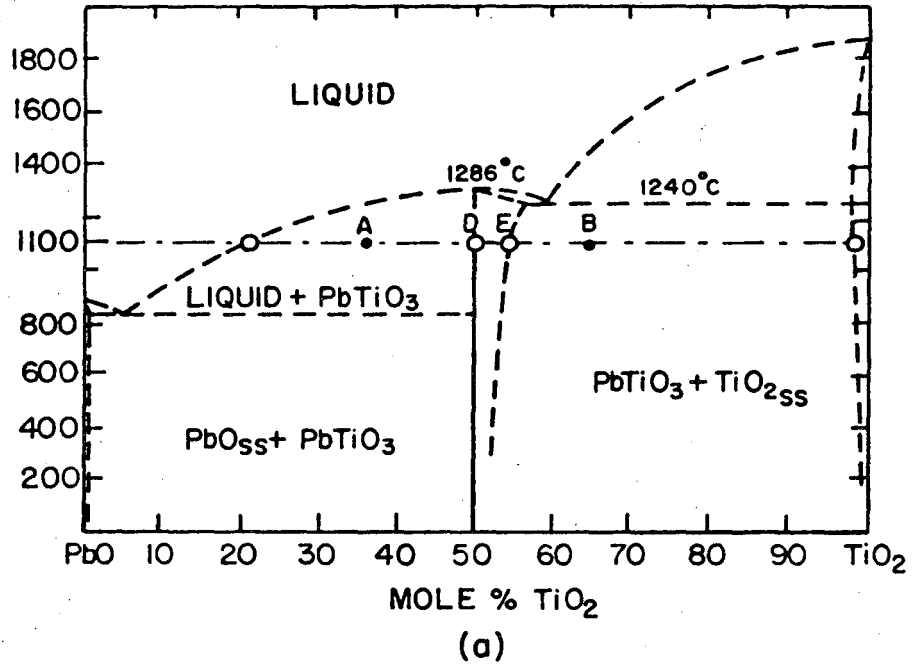
- Fig. 12. Lead oxide and zirconia activity as a function of composition in the lead zirconate single-phase region as determined from analysis of the Knudsen effusion experimental data and a graphical integration of the Gibbs-Duhem equation.
- Fig. 13. The free energy of mixing PbO and either TiO_2 or ZrO_2 as a function of composition in either the lead titanate or the lead zirconate single-phase region.
- Fig. 14. Natural log of vapor pressure (PbO) vs $1000/T^\circ\text{K}$ as determined by the Knudsen Effusion experiments. (This data is least squares fitted to a linear form and is compared to the thermochemical data and the results of another Knudsen experiment.)
- Fig. 15. \log_e (lead oxide vapor pressure) vs $1000/T^\circ\text{K}$ for lead titanate in equilibrium with a lead rich liquid and with titania. The results are compared to those for pure lead oxide.
- Fig. 16. \log_e (lead oxide vapor pressure) vs $1000/T^\circ\text{K}$ for lead zirconate in equilibrium with a lead rich liquid and with zirconia. The results are compared to those for pure lead oxide.
- Fig. 17. Lead oxide activity as a function of reciprocal temperature ($1000/T^\circ\text{K}$) for all experimental Knudsen effusion vapor pressure data: $a_{\text{PbO}}(\text{PZT}) = P_{\text{PbO}}(\text{PZT})/P_{\text{PbO}}(\text{pure})$.
- Fig. 18. Lead oxide activity as a function of $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})_3\text{O}_3$ when the PZT compound is in equilibrium with a lead rich liquid: 0 - refer to experimentally determined points, X - refers to extrapolated points.

Fig. 19. The activity coefficient of lead oxide as a function of $\text{PbTi}_x\text{Zr}_{1-x}\text{O}_3$ composition at 1100°C and 1200°C, calculated from the experimental Knudsen data showing a deviation from Raoult's law.



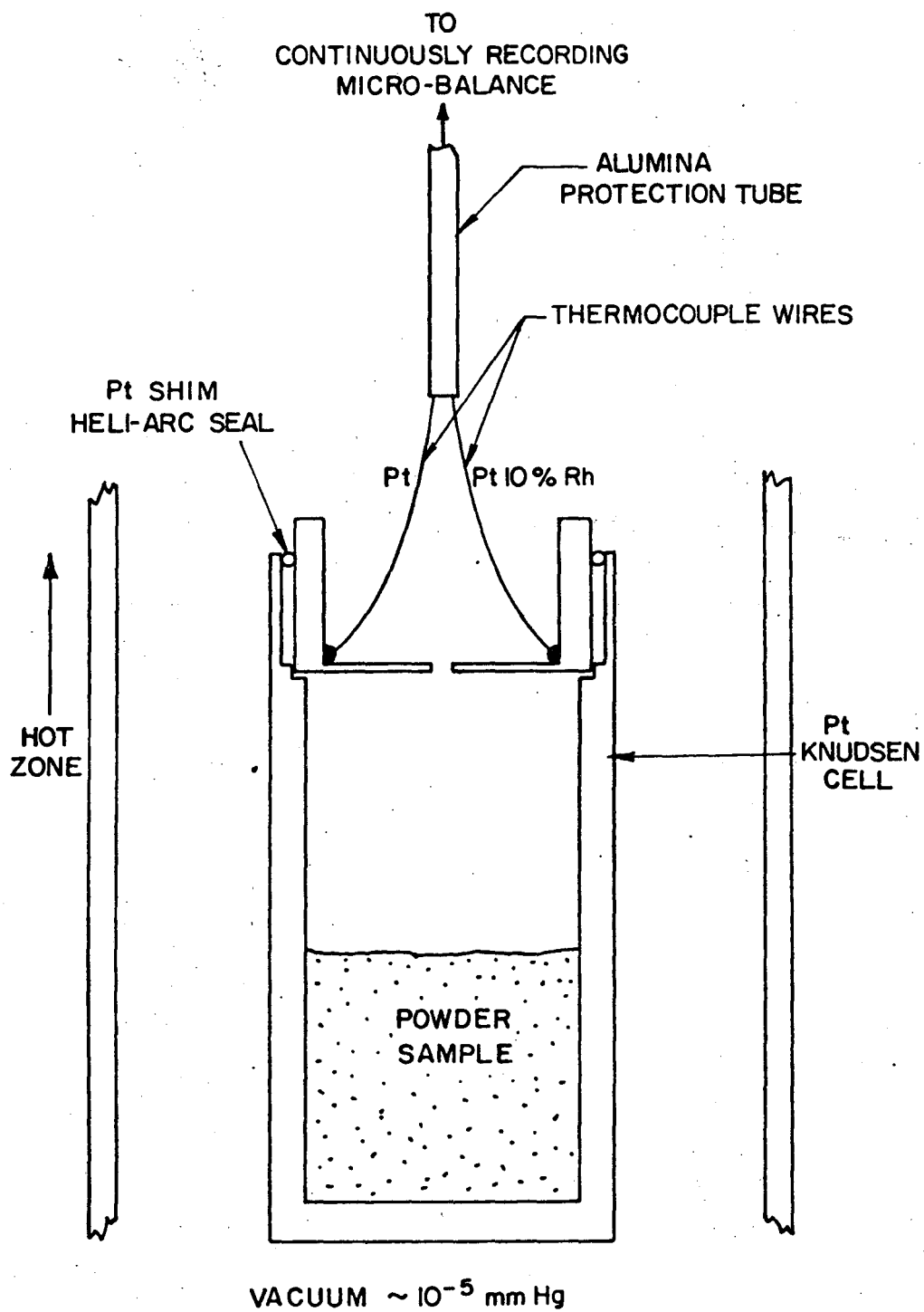
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Fig. 1



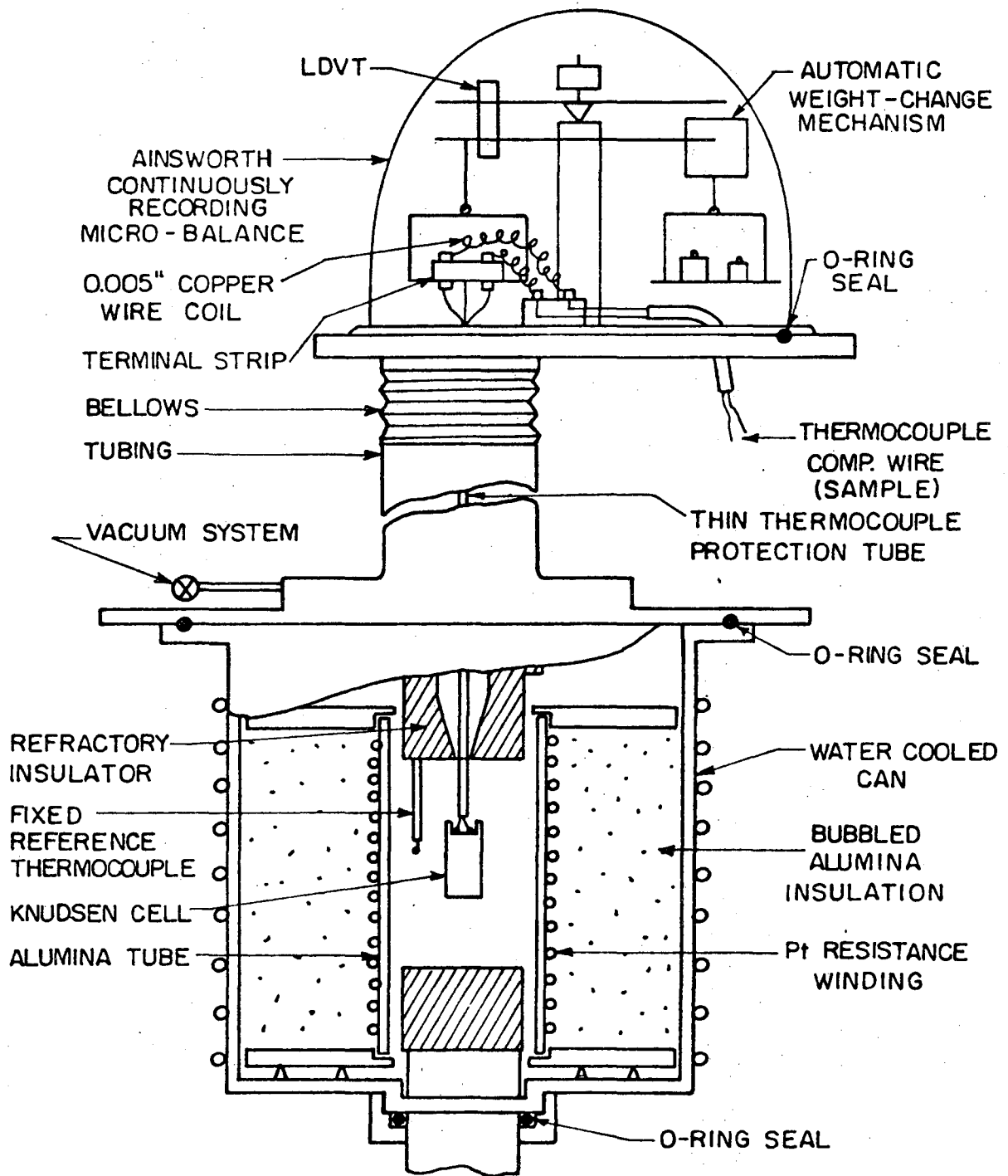
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Fig. 2



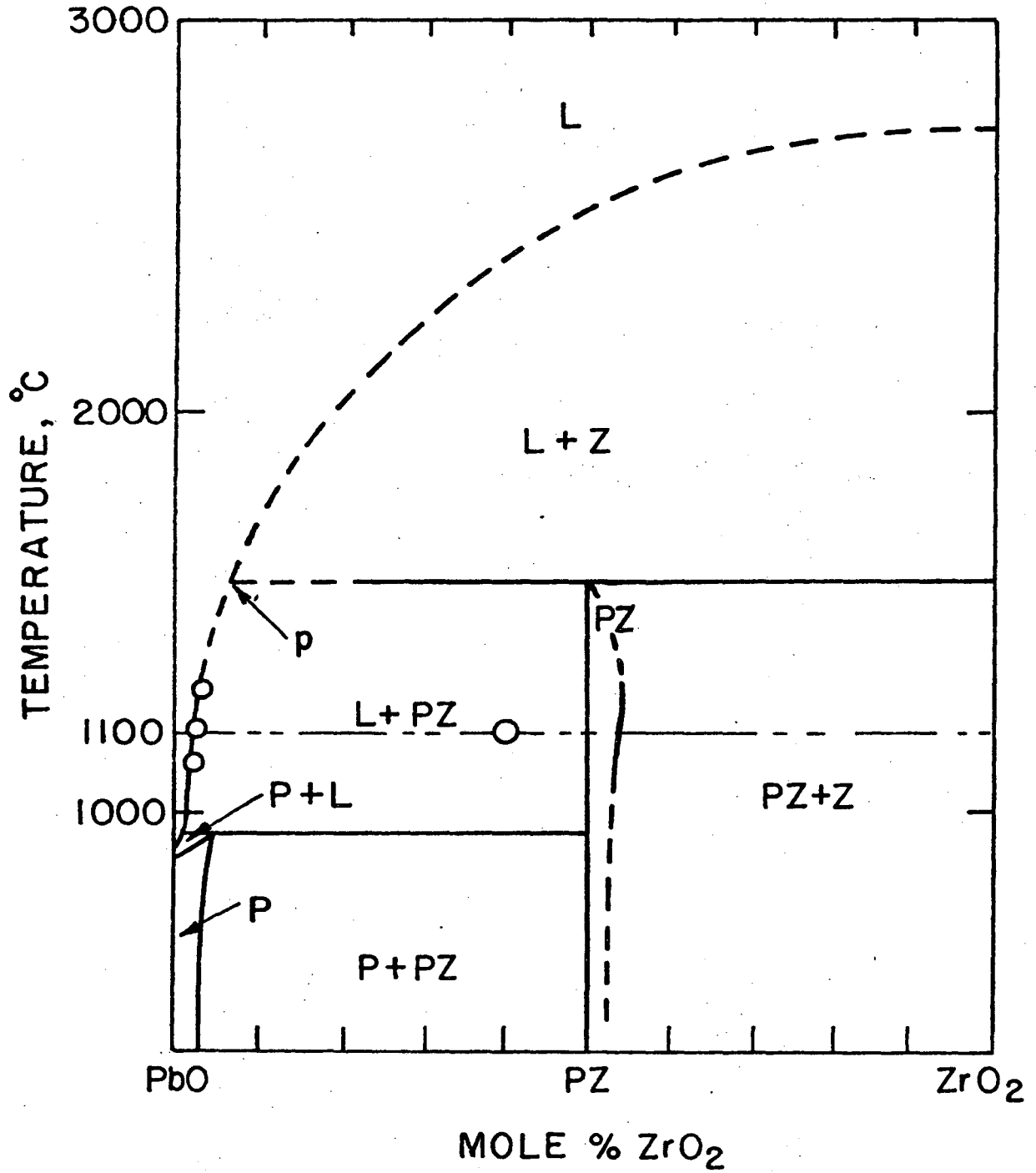
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Fig. 3



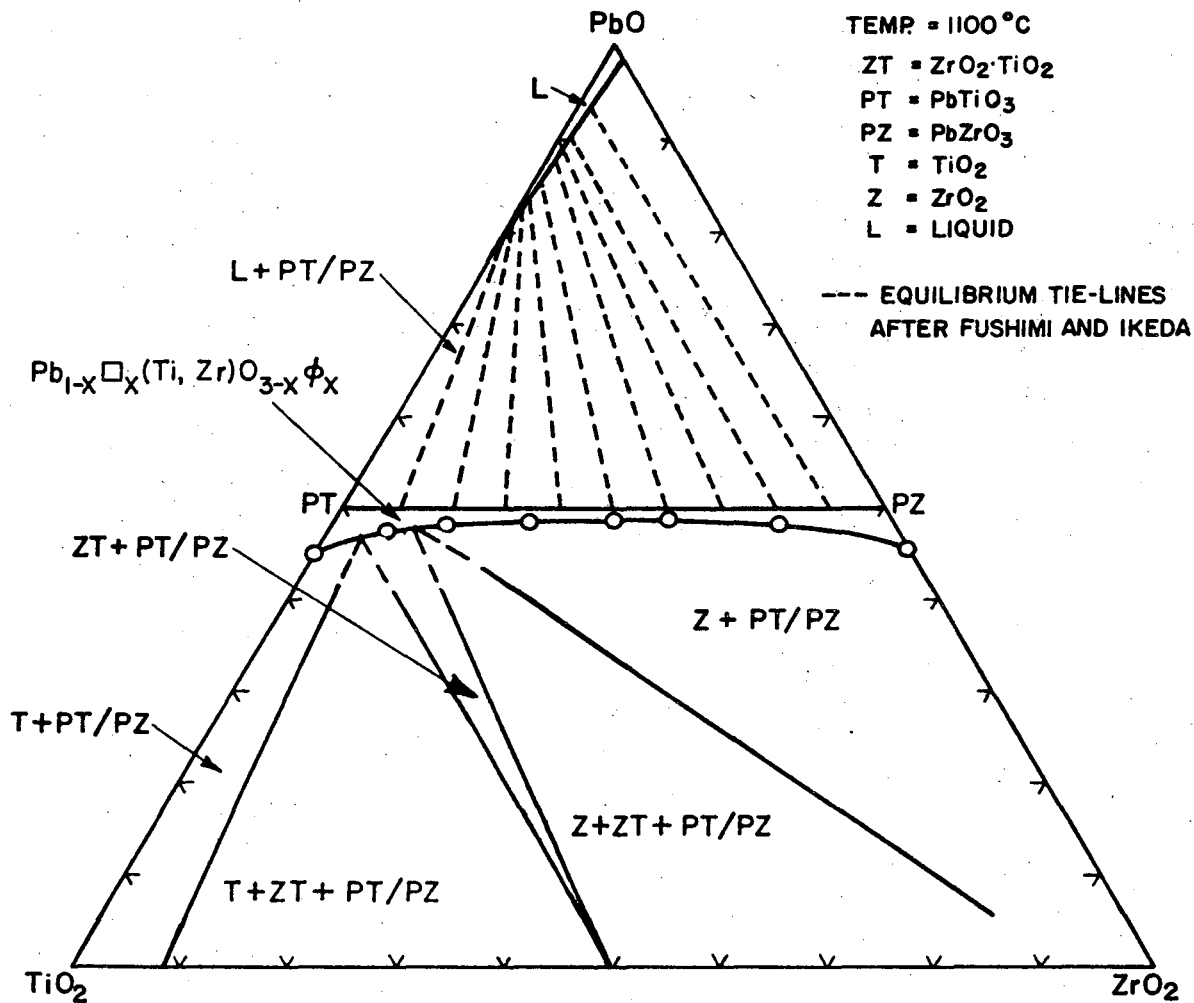
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Fig. 4



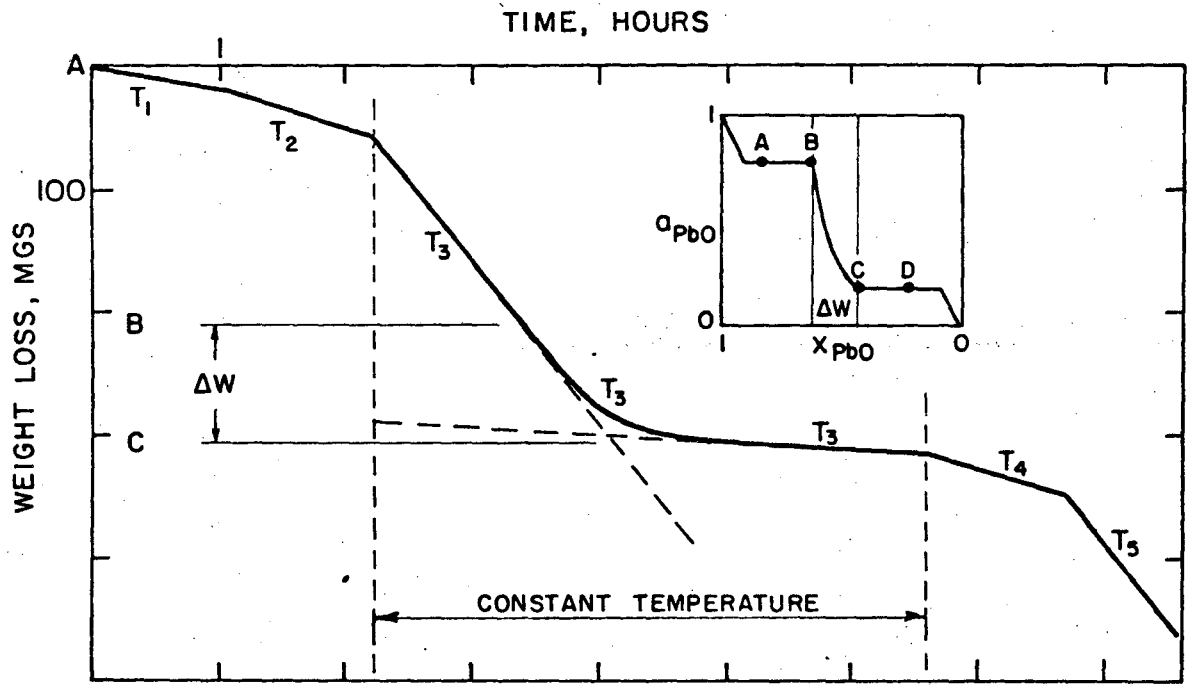
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Fig. 5



XBL726-644I

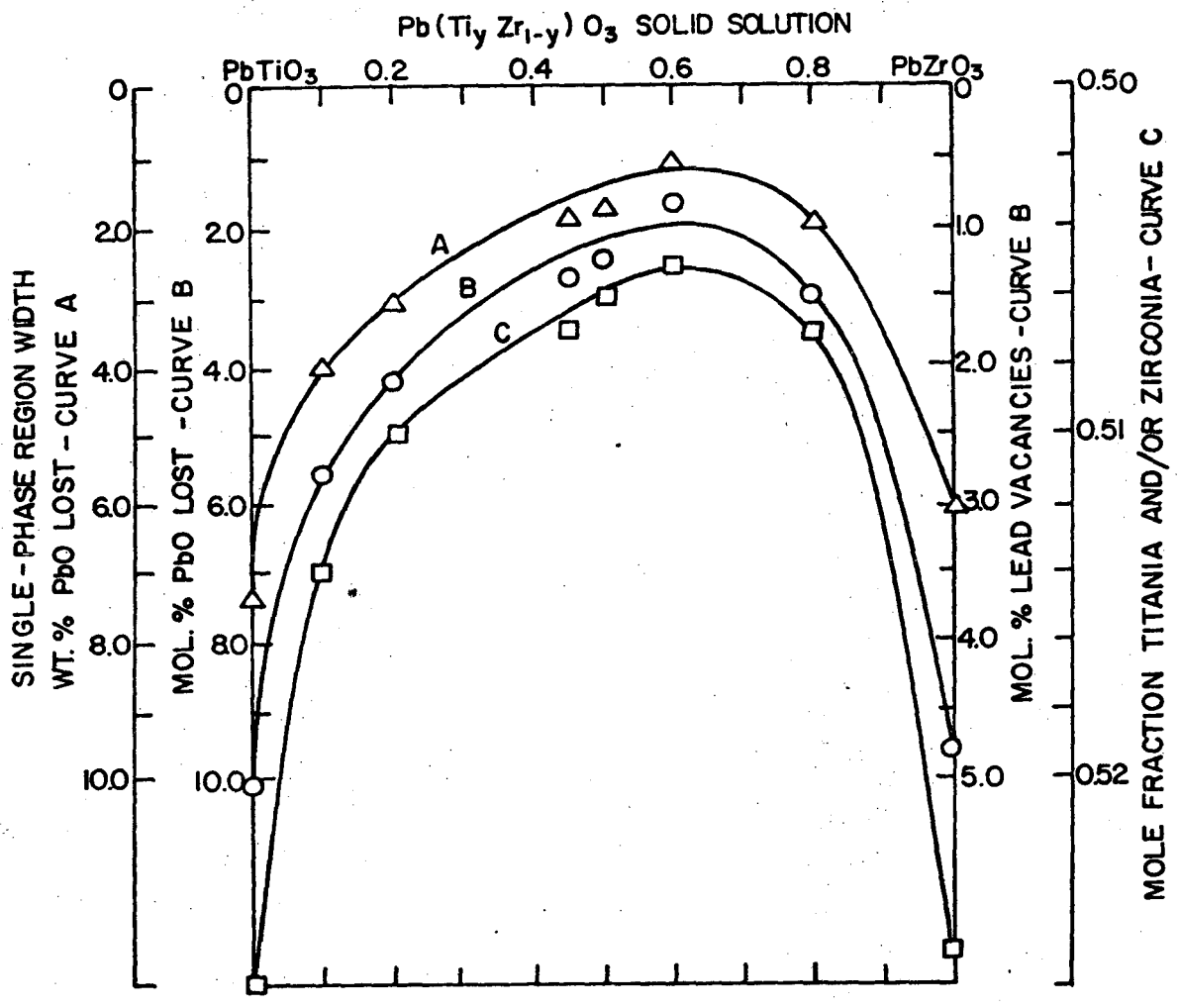
Fig. 6



TYPICAL WEIGHT LOSS DATA FROM KNUDSEN EFFUSION EXPERIMENT ON
 $(Pb(Ti_xZr_{1-x})O_3 + \delta PbO)$

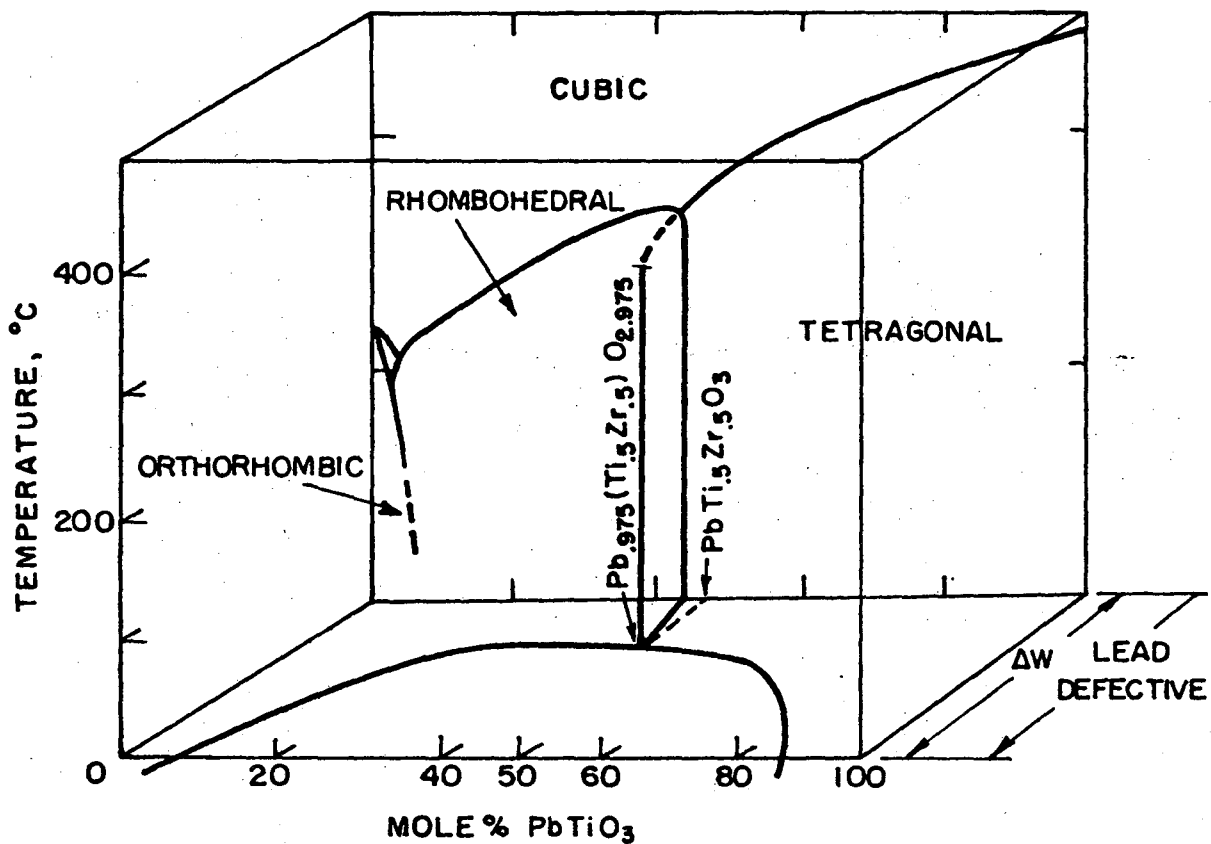
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Fig. 7



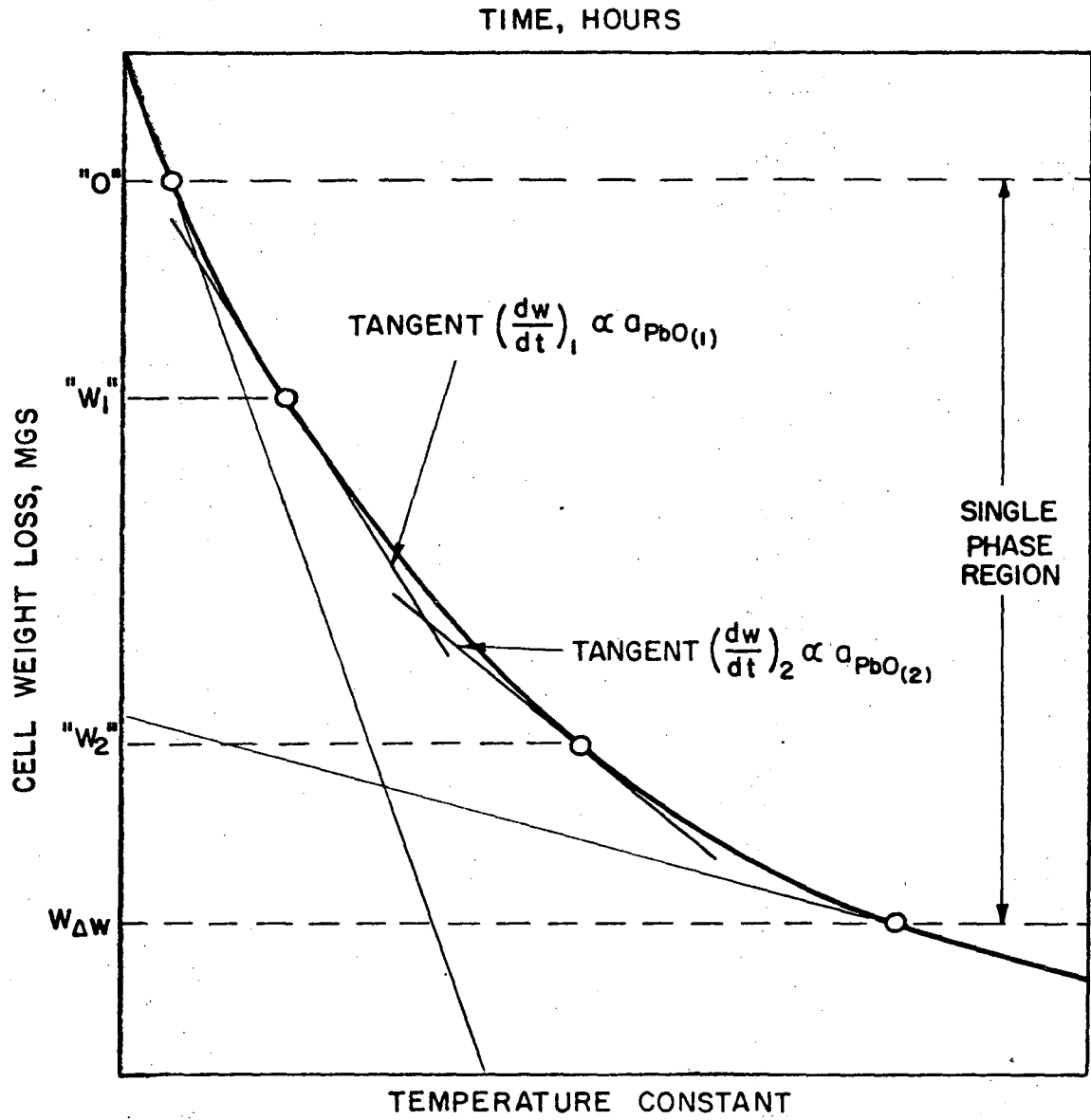
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Fig. 8



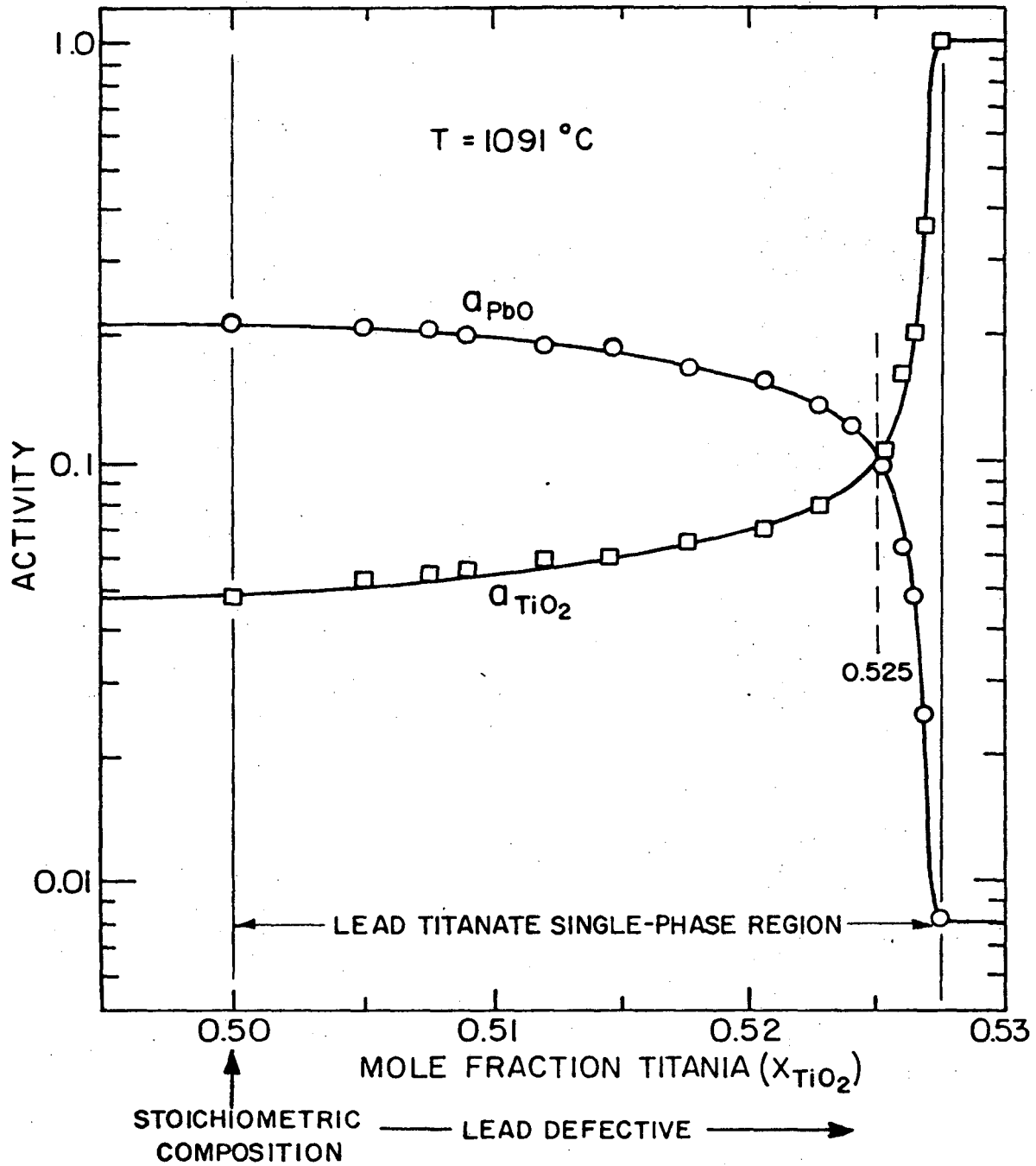
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Fig. 9



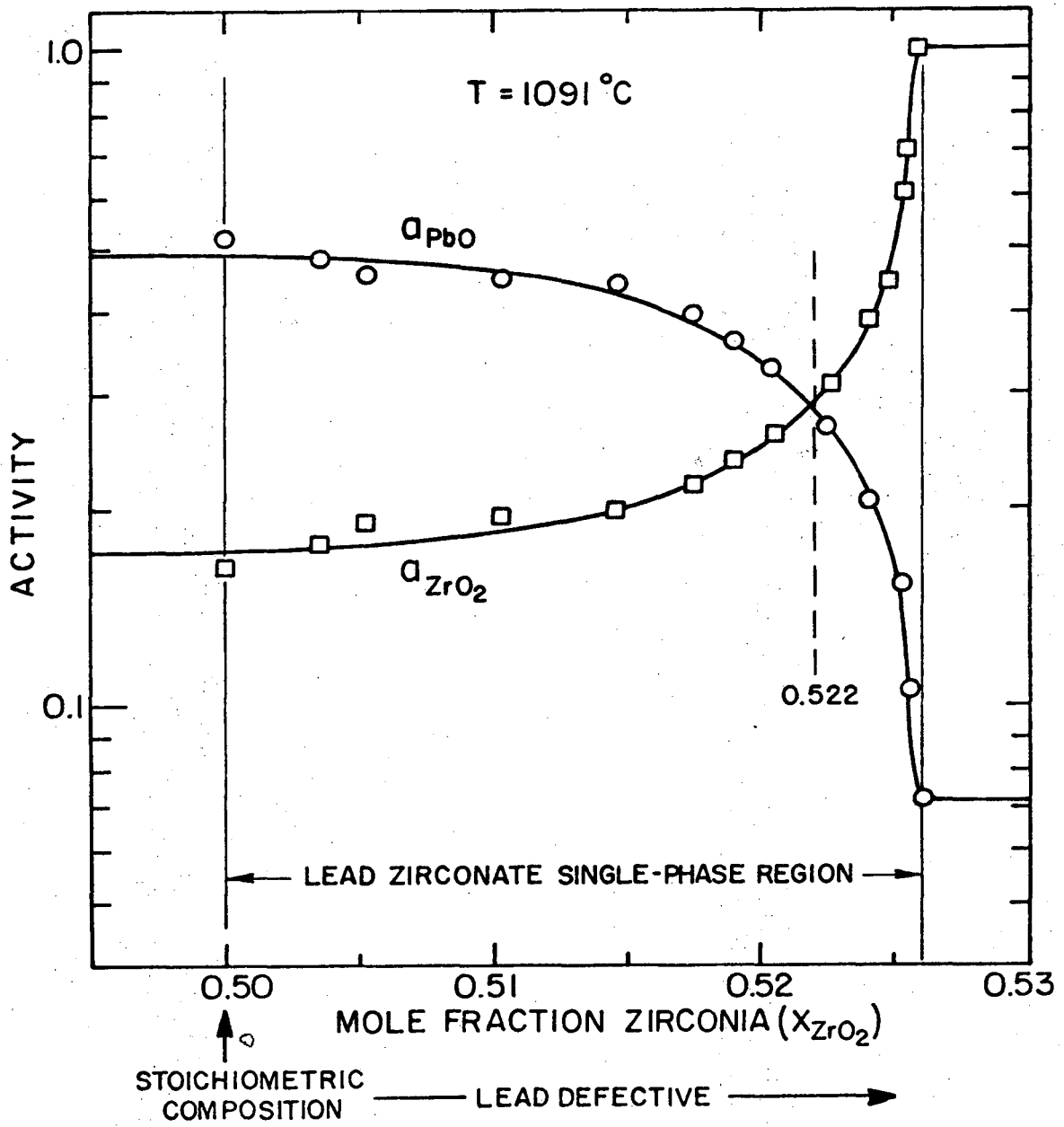
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Fig. 10



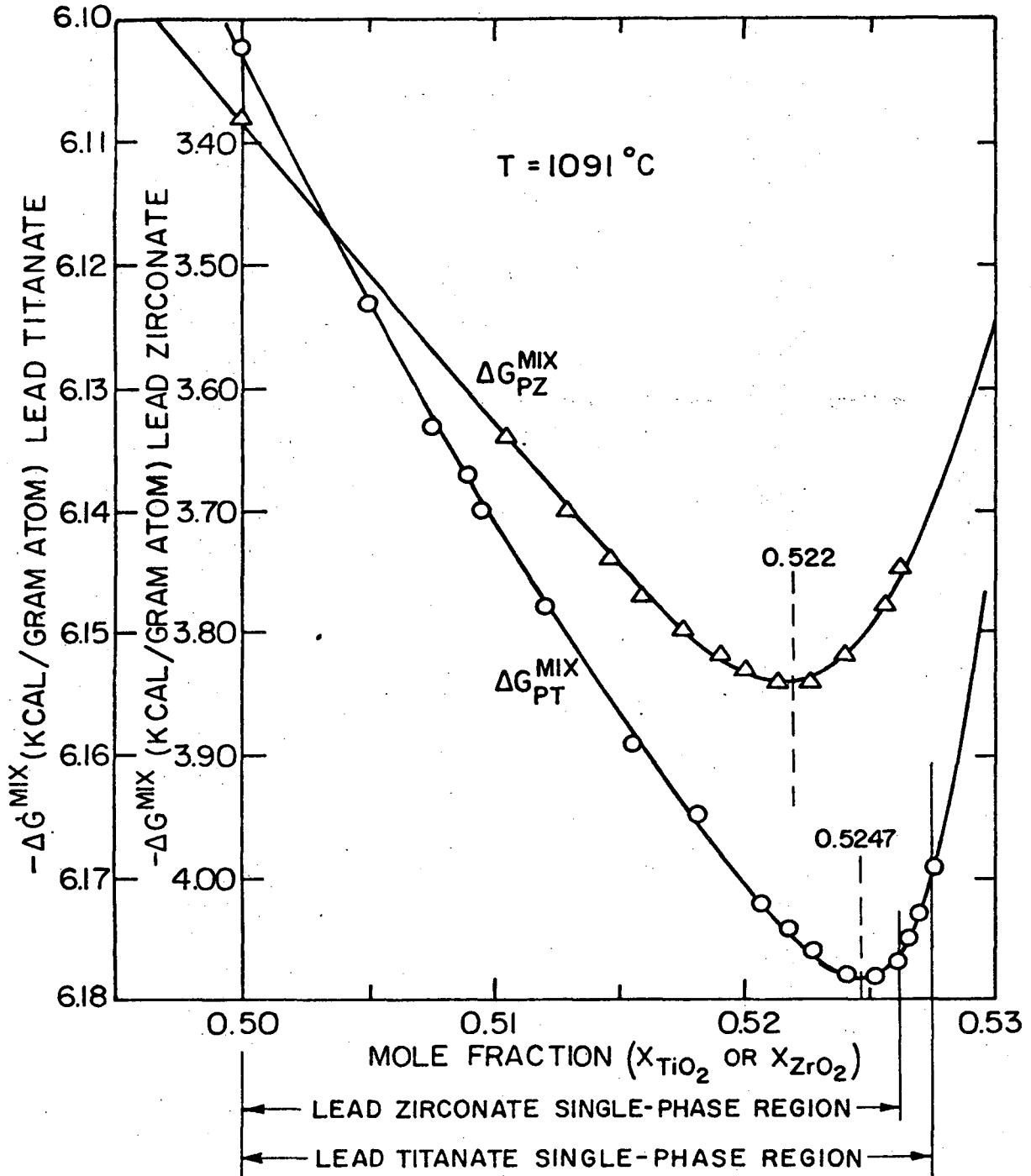
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Fig. 11



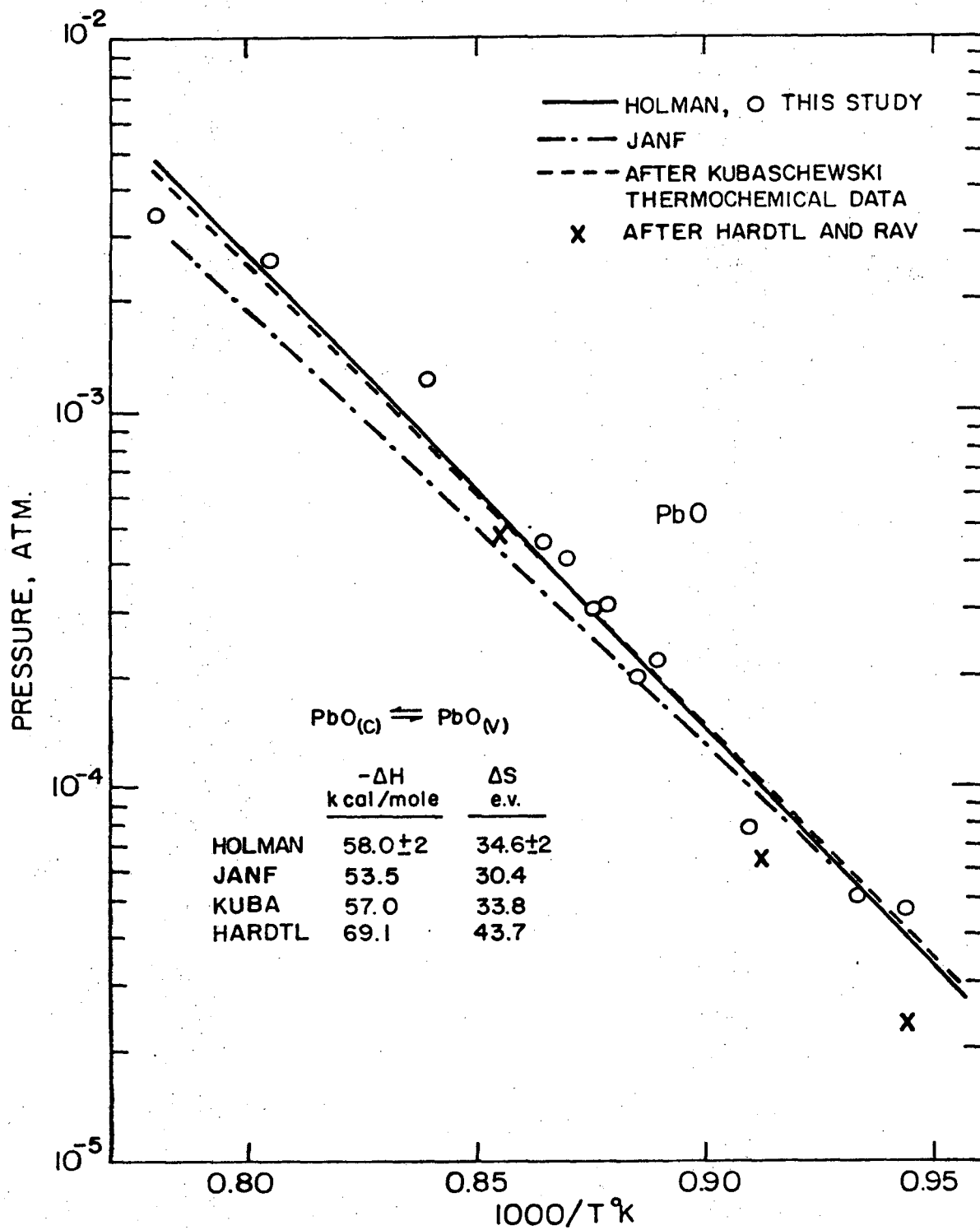
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Fig. 12



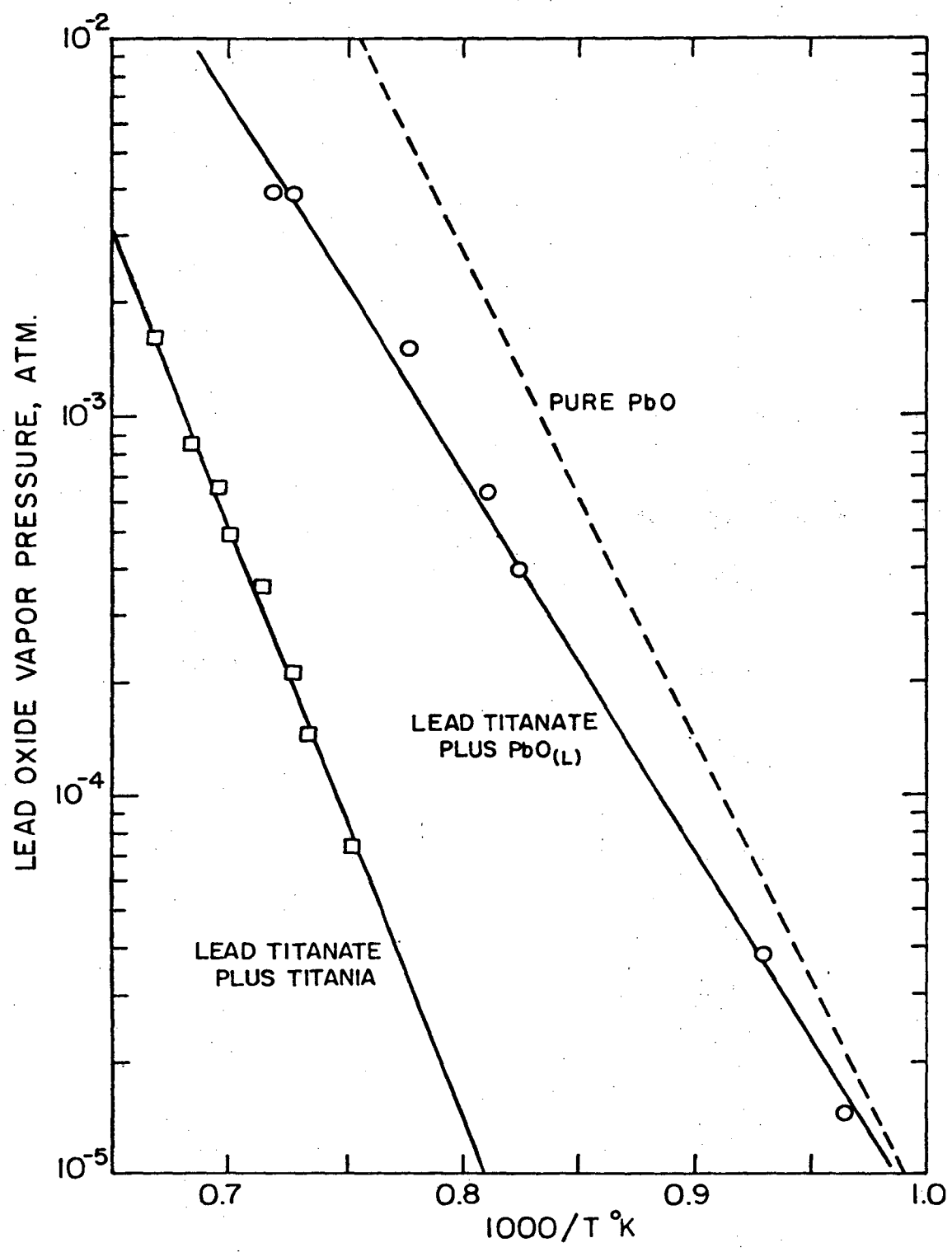
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Fig. 13



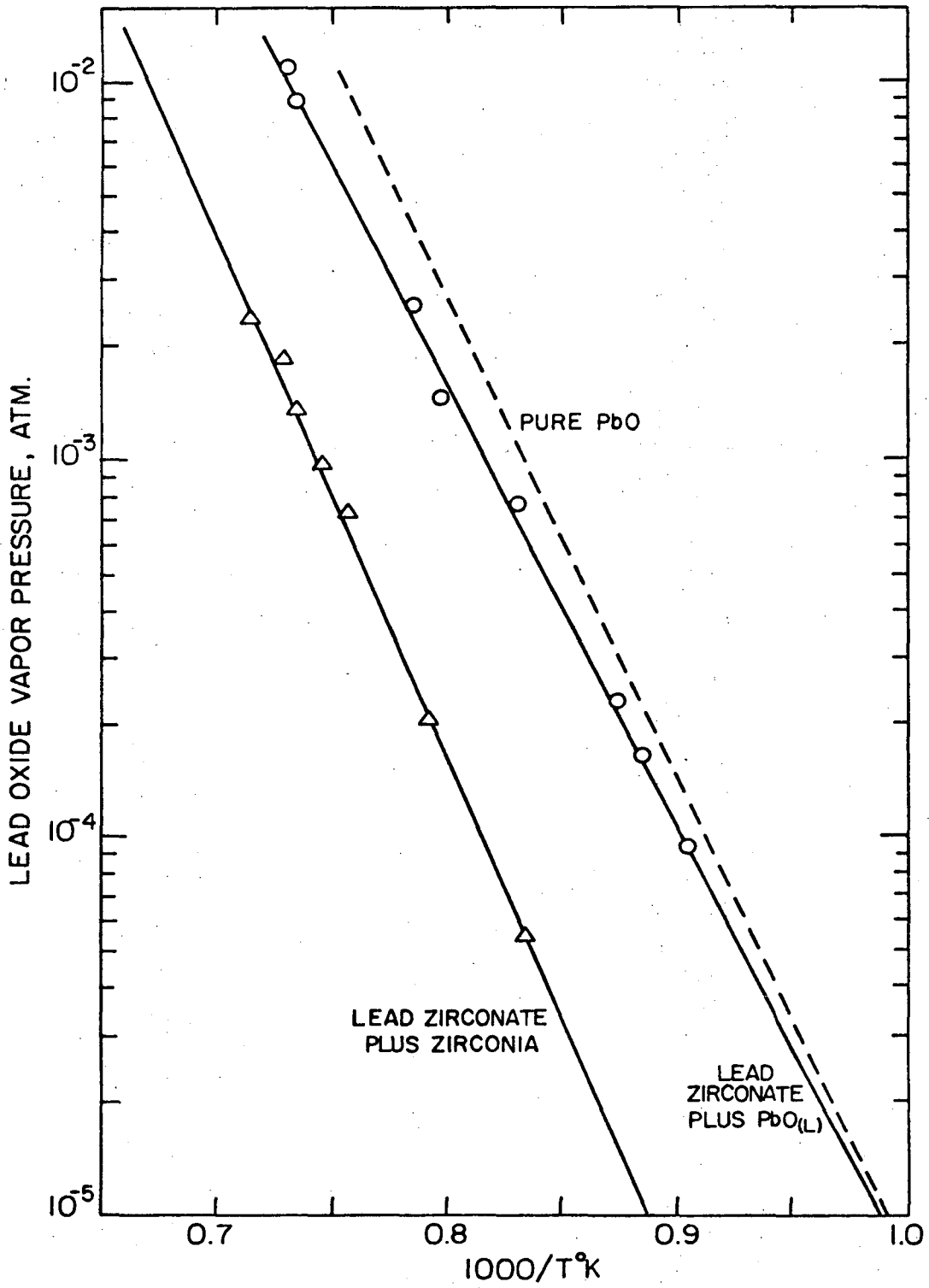
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Fig. 14



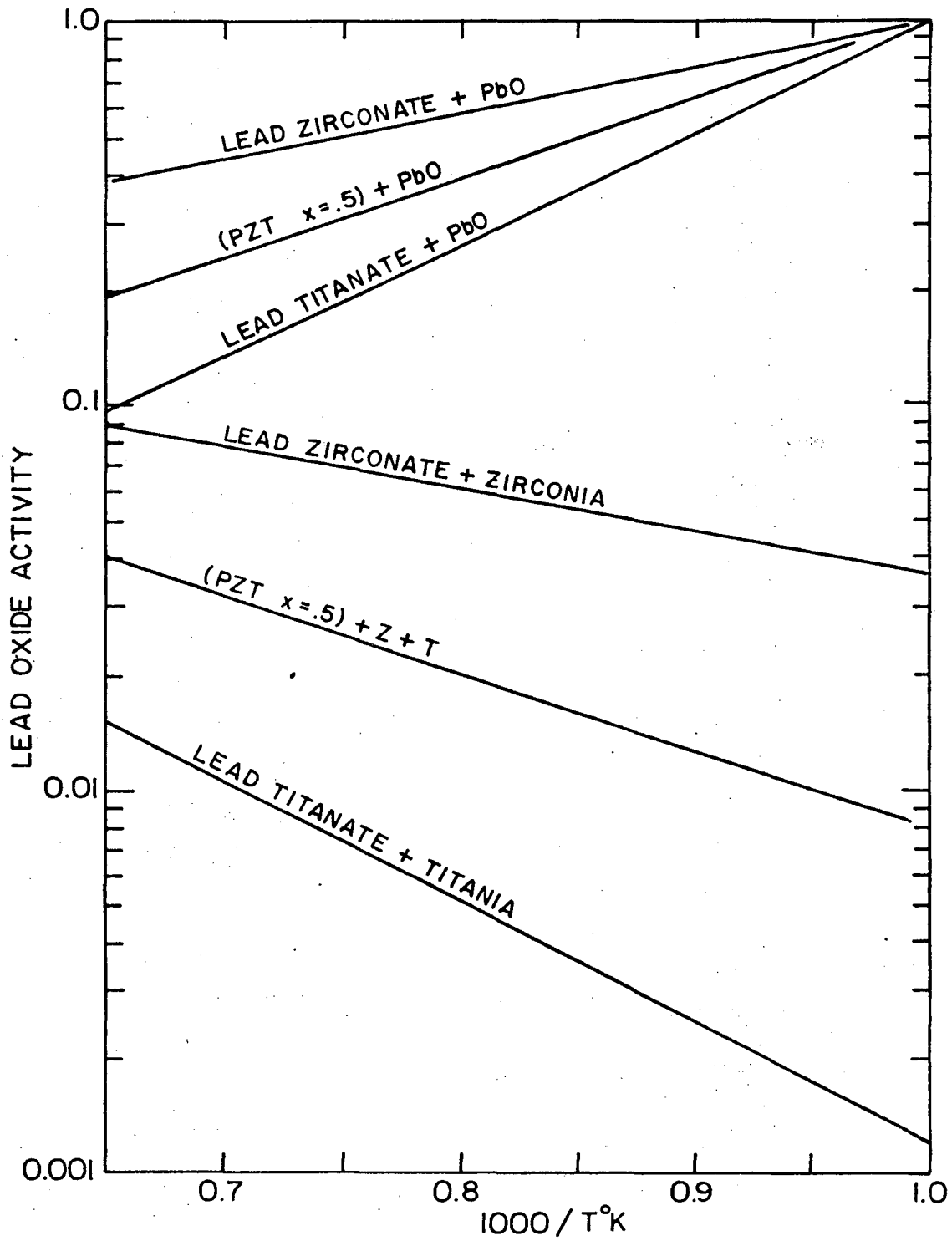
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Fig. 15



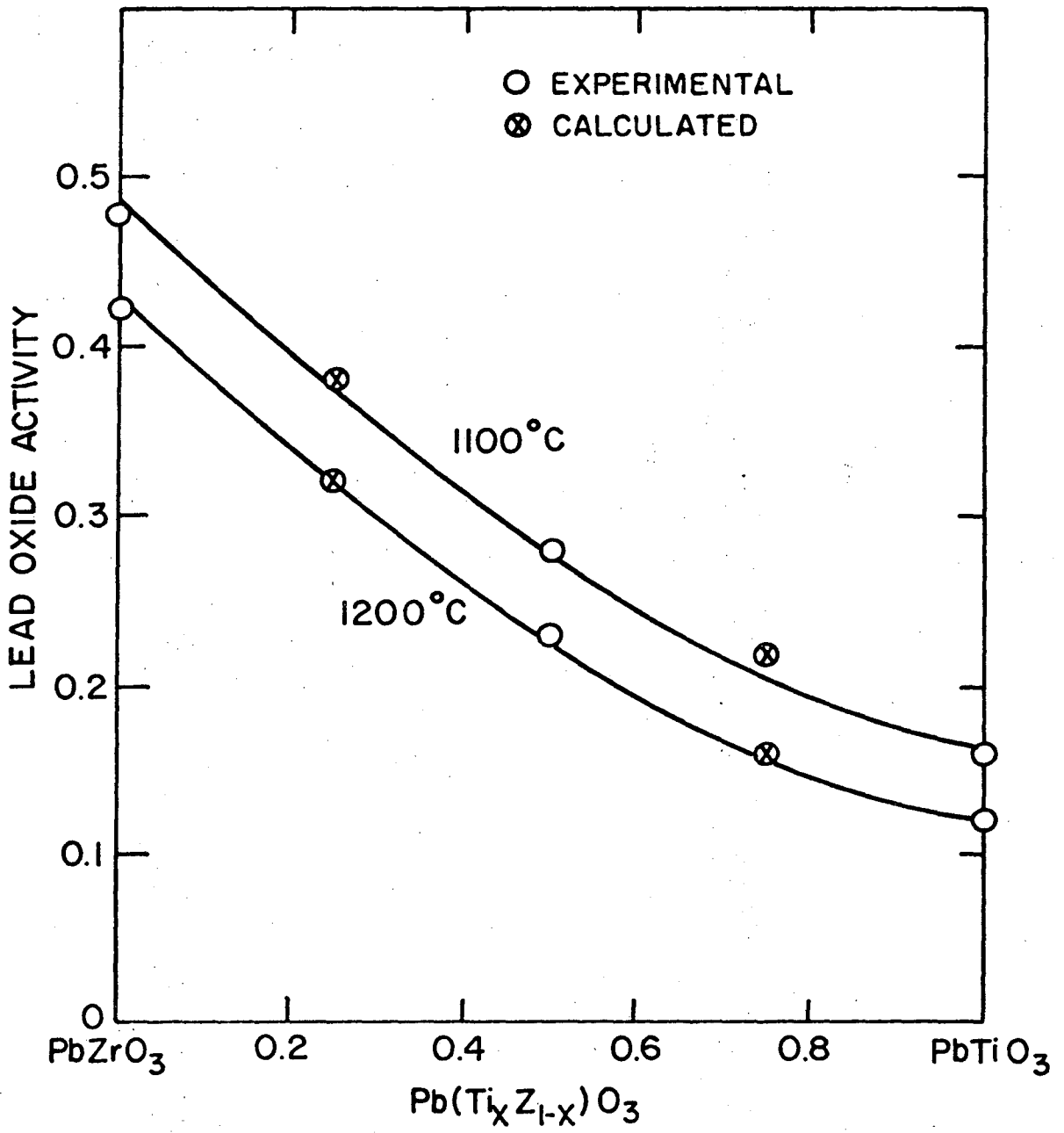
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Fig. 16



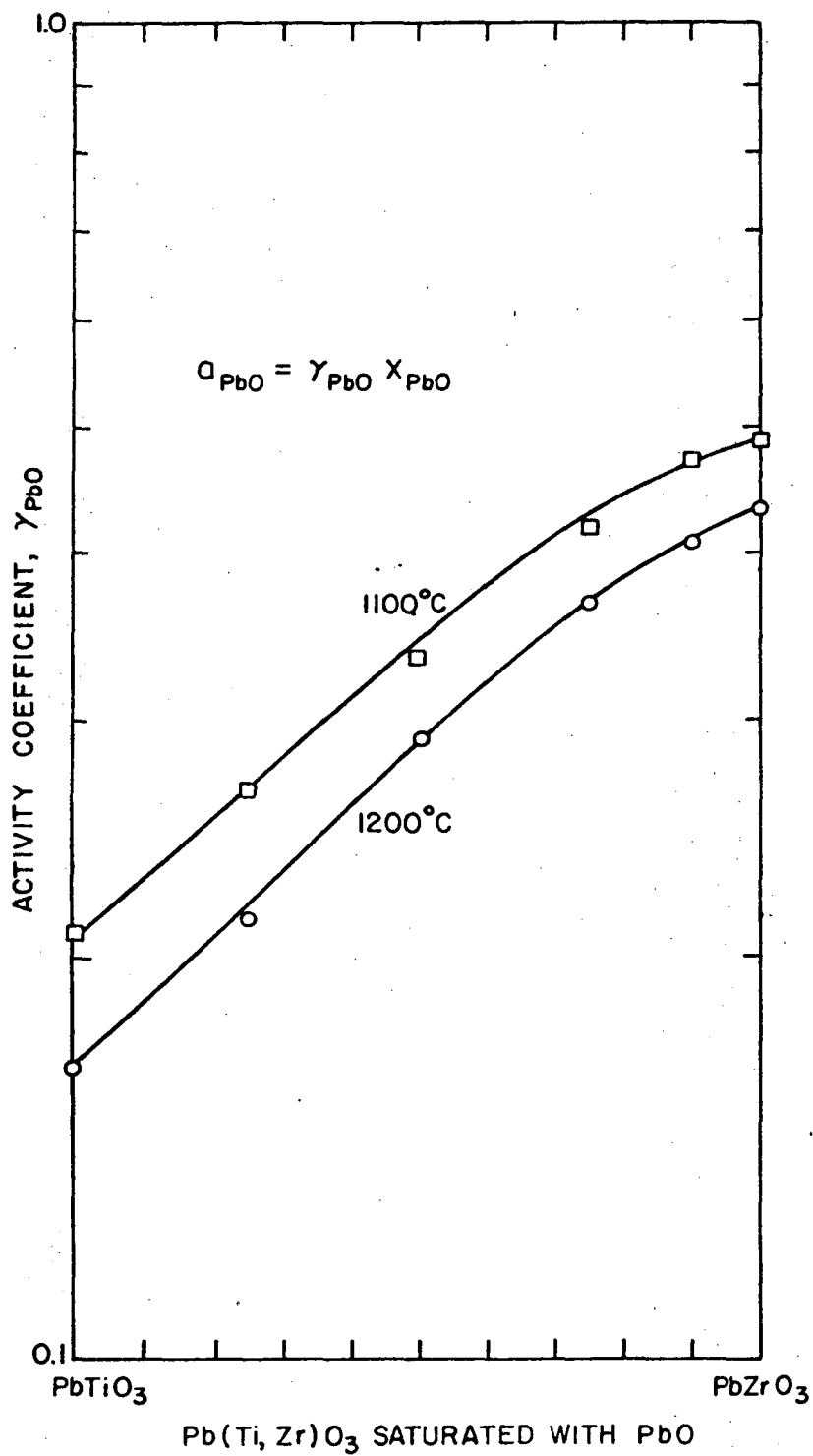
XBL 726-6442

Fig. 17



XBL726-6437

Fig. 18



XBL726-6434

Fig. 19

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