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PART XXVI

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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART XXVI. MASS SPECTROMETRIC STUDY OF THE VAPORIZATION OF LEAD MONOXIDE. THE DISSOCIATION ENERGY OF PbO

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PART XXVI

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF61(052)-764. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-graphitic." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

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ABSTRACT

The composition of the vapor in equilibrium with lead oxide (yellow rhombic form) in the temperature interval 1000-1150°K was determined mass spectrometrically. The predominant species are PbO, Pb₂O₂, Pb₃O₃ and Pb₄O₄.

From the partial PbO pressure measured here and that based on a reinterpretation of the literature data, when taking the presence of the polymers into account, the dissociation energy of the molecule PbO was calculated:

$$D_0^{\circ}(\text{PbO}) = 88.4 \pm 1.4 \text{ kcal/mole.}$$

The enthalpy H_{298}° of the reactions



is 63.4±4, 126.4±6.0 and 202.0±10.0 kcal/mole respectively.

This technical documentary report has been reviewed and is approved.



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MASS SPECTROMETRIC STUDY OF THE VAPORIZATION OF
LEAD MONOXIDE^M
THE DISSOCIATION ENERGY OF PbO

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1. INTRODUCTION.

Previous mass spectrometric studies⁽¹⁻⁹⁾ of the vaporization of Group IV(Me)-Group VI(X) compounds have shown the presence in the vapor of these compounds of polymeric molecules $(MeX)_n$. The relative partial pressure of these gaseous species is particularly high for the oxides and increases when going from $Si(s) + SiO_2(s)$ ⁽¹⁾ to $GeO(s)$ ⁽⁷⁾ and to $Sn(s) + SnO_2(s)$ ⁽⁸⁾. It was therefore believed that in the case of $PbO(s)$, their contribution to the total vapor pressure would be even larger and that these molecules would probably become the major components of the vapor, which was confirmed in preliminary measurements⁽⁸⁾. Knacke and Prescher⁽¹⁰⁾ were lead to a similar conclusion when comparing the difference between the heats of sublimation and evaporation of lead monoxide, 14.5 kcal/mole, with the heat of fusion, 6.6 kcal/mole.

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Measurements of the total vapor pressure of PbO(s) have been carried out by several authors⁽¹⁰⁻¹⁶⁾ using either Knudsen, Langmuir or flow techniques. These measurements cover the temperature range extending from 1808 (boiling point)⁽¹⁰⁾ to 887°K where the total pressure is approximately 10^{-7} atmospheres. In this temperature range the yellow rhombic form β is the stable one below the melting point, 1170±4°K. The red tetragonal form becomes unstable at 762°K.

Although the molecule PbO has been the object of spectroscopic investigations^(17,18), no spectroscopic value for the dissociation energy has been proposed other than that based on the linear Birge Spomer extrapolation for the ground state leading to $D_0^{\circ}(\text{PbO}) = 4.3$ ev.

The present work reports the details of the mass spectrometric study of the vaporization of PbO(s) , $\text{Pb(s)} + \text{PbO(s)}$ and $\text{PbO}_2\text{(s)}$ which leads to the determination of values for the dissociation energy of PbO and for the stability of the gaseous molecules Pb_2O_2 , Pb_3O_3 and Pb_4O_4 .

2. EXPERIMENTAL.

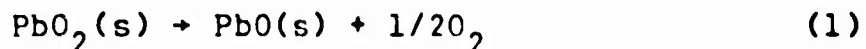
The mass spectrometer used is a single focussing 60° sector, 20 cm radius of curvature instrument described previously^(19,20). The experimental set-up⁽²¹⁾ and the principle of the thermodynamic study⁽²²⁾ of vaporization processes was also given previously.

In the study, commercial samples of yellow PbO, PbO₂ and powdered Pb were used. The PbO samples were of the yellow rhombic^{form.} Zirconia and platinum were found to be satisfactory containers for PbO and PbO₂ while a nickel crucible was used for the mixture Pb(s) + PbO(s).

Temperature were measured both with a Pt-Pt 10% Rh thermocouple and with an optical pyrometer.

3. COMPOSITION OF THE VAPORS.

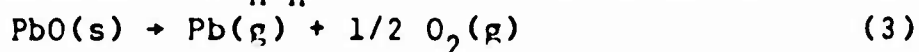
Samples of PbO₂(s) heated to approximately 400°K gave rise to a decomposition reaction leading to the formation of a lower oxide and O₂ molecules. On further heating the samples to approximately 1050°K they vaporized in the same way as PbO(s). It is however possible that the transformation



occurs through intermediate steps corresponding to the formation of either Pb₂O₃(s) or Pb₃O₄(s) or maybe both.

The ions characterized of the PbO(s) system identified by their mass and isotopic distribution and shown to be produced from neutral species originating from the cell by use of a movable beam defining slit are given in Table 1 together with the relative ion intensities for the highest temperature of the experiments. Ionization efficiency curves were measured for several of these ions. The approximate appearance potentials, given in Table 1, were obtained by the linear extrapolation

method, the energy scale being calibrated with the known appearance potentials of $\text{H}_2\text{O}^{+ (23)}$ and $\text{Hg}^{+ (24)}$ ions. The ionization efficiency curve of Pb^+ showed that two processes lead to the formation of this ion. The first appearance potential of Pb^+ (7.3 ± 0.5 eV) agrees with the ionization potential of lead⁽²⁴⁾ (7.4 eV) and is therefore attributed to direct ionization of atomic lead. The second (15.7 $\pm$ 1.0 eV) is attributed to fragmentation of the molecular species $(\text{PbO})_n$ ($n = 1$ up to 4). From the measured appearance potentials of the other ions it is concluded that PbO^+ , Pb_2O_2^+ , Pb_3O_3^+ and Pb_4O_4^+ are parent ions while the high appearance potentials of Pb_2O^+ and Pb_3O_2^+ indicate these ions to be result of fragmentation of the higher polymers. Although no appearance potential for the Pb_2^+ ion was measured, it can be concluded from thermodynamic considerations that it is a fragment ion. At the highest temperature reached in these experiments, small intensities were detected at masses corresponding to Pb_5O_5^+ ($M=1116$) and Pb_6O_6^+ ($M=1340$). It was unfortunately not possible to measure appearance potentials for these ions because of their low intensity. PbO vaporizes thus according to the reactions



4. PRESSURE DETERMINATIONS.

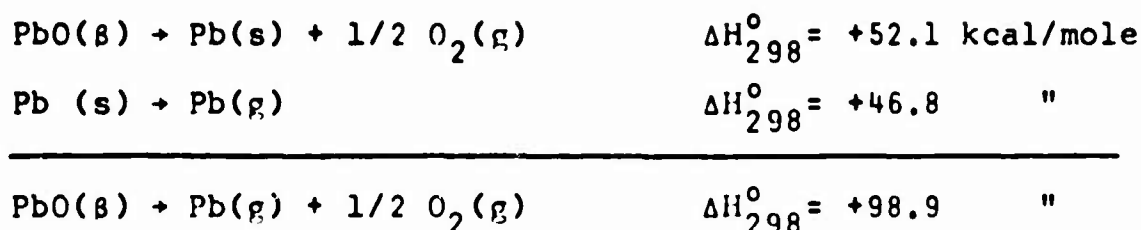
To determine the pressures of PbO(g) (Table 2) over lead monoxide three different methods were applied.

In the experiments 09-20, -21 and -30 pressures were normalized relative to the calculated decomposition pressure of PbO(s) . The latter was computed from the known heat of formation of PbO(s) , $\Delta H_{298, f}^\circ = -52.1$ kcal/mole⁽²⁵⁾ and the

TABLE 1. Appearance Potentials AP and Relative Ion Intensities I (at 1200°K)

Ion	Pb ⁺	PbO ⁺	Pb ₂ ⁺	Pb ₂ O ⁺	Pb ₂ O ₂ ⁺	Pb ₃ O ₂ ⁺	Pb ₃ O ₃ ⁺	Pb ₄ O ₄ ⁺	Pb ₅ O ₅ ⁺	Pb ₆ O ₆ ⁺
A.P. (in eV)	7.3±0.5 and 15.7±1.0	9.0±0.5	-	11.9±1.0	8.8±0.5	14.6±1.0	9.7±1.0	8.5±1.0	-	-
I	1.20	1.00	8.4×10 ⁻²	4.5 10 ⁻²	1.19	9.0×10 ⁻²	1.2×10 ⁻¹	1.30	9.2×10 ⁻³	1.95×10 ⁻²

following cycle



It was taken into account that for Knudsen effusion

$$p(\text{Pb})/p(\text{O}_2) = 2(M_{\text{Pb}} + M_{\text{O}_2})^{1/2} \quad (4)$$

The numerical values for the free energy function of $\text{PbO}(\text{s})$, $\text{O}_2(\text{g})$ and $\text{Pb}(\text{g})$ were taken from the literature⁽²⁵⁻²⁷⁾. The partial pressures of the other species were obtained from the relation

$$\frac{P_1}{P_2} = \frac{I_1 \sigma_2 (E - A_2/A_2) \gamma_2 T_1}{I_2 \sigma_1 (E - A_1/A_1) \gamma_1 T_2} \quad (5)$$

where P is the partial pressure in atmosphere, I is the ion intensity in arbitrary units, σ is the relative ionization cross section at the maximum of the ionization efficiency curve, A is the appearance potential in eV, E is the energy of the ionizing electrons in eV, γ is the secondary electron multiplier efficiency and T is the absolute temperature. σ values were estimated on the basis that the ionization cross section for a dimer is 1.6 times that of a monomer which was shown to hold for several diatomic⁽²⁸⁾ and dimeric molecules⁽²⁹⁾. Values of atomic ionization cross sections were taken from Otvos and Stevenson⁽³⁰⁾. Multiplier efficiencies were taken from the calibration curve⁽³¹⁾ of a multiplier similar to the one used in this work, molecular effects on the first dynode being taken into account⁽³²⁾. The numeric values used are $\sigma\gamma = 0.50; 1.00; 1.00; 1.30; 1.51; 1.69; 1.90$ and 2.10 for O_2 , Pb , PbO , Pb_2O_2 , Pb_3O_3 , Pb_4O_4 , Pb_5O_5 and Pb_6O_6 respectively.

In the experiment (1402) a sample of PbO(s) of known weight was vaporized completely, the intensities of the major species (PbO, Pb₂O₂, Pb₃O₃ and Pb₄O₄) being monitored and integrated with time. The use of the Hertz-Knudsen relation leads to a pressure determination as described previously^(7,22).

In the experiment 14-01 carried out with a mixture of Pb(s) and PbO(s), the pressure of Pb assumed, in view of the low solubility of oxygen in lead⁽³³⁾, to be present at essentially unit activity, was used as the pressure standard in relation(6).

5. RESULTS.

a. Enthalpy of sublimation of PbO.

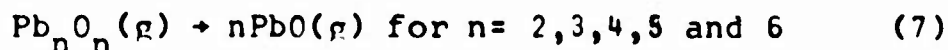
The heat of sublimation of PbO(g) was calculated from the partial pressures determined as described above by using the relation

$$\Delta H_{298,s}^{\circ}(\text{PbO}) = -RT \ln P_{(\text{PbO})} + T \Delta(G^{\circ} - H_{298}^{\circ}/T) \quad (6)$$

The values are given in table 2. The numerical values of the free energy functions ($G^{\circ} - H_{298}^{\circ}/T$) for PbO(s) and PbO(g) were taken from the literature⁽²⁷⁾. The mean value is $\Delta H_{298}^{\circ}(\text{sub}, \text{PbO}_{\beta}) = 69.2 \pm 1.3$ kcal/mole.

b. Stability of Pb_nO_n polymer.

The equilibrium constants for the reactions



are given in fig.1. Polymer to monomer ratios obtained in one experiment where no calibration was carried out are included in fig.1 using PbO partial pressures based on the heat of sublimation obtained above. The enthalpy changes for reaction (7) were derived, in the case of Pb₂O₂, Pb₃O₃ and Pb₄O₄, from least square treatments which give

TABLE 2. Enthalpy of Sublimation of PbO(g)

Exp.n°	System	T (°K)	- logp(PbO) (atm)	ΔH_{298}^0 (kcal/mole)
0920	PbO _g	1020	6.11 (±1.0)	68.6 (±1.0)
		1030	6.13	69.4
		1100	5.40	70.2
0921	PbO _g (initially PbO ₂)	1068	5.32	67.8
		1041	5.66	67.9
		1017	6.11	68.4
		998	6.56	69.2
0930	PbO _g	1088	5.35	69.1
		1114	5.12	68.4
		1149	4.91	70.5
1401	Pb+PbO _g	1003	6.68	70.2
		1023	6.29	69.4
		1063	5.65	69.2
		1070	5.40	68.2
1402	PbO _g	1046	5.91	69.5
		1065	5.73	69.7
		1110	5.18	69.6
		1126	4.99	69.6
				69.2

standard deviation ±0.8

overall uncertainty ±1.3

$$\Delta H_{1040}^{\circ} = 61.4 \pm 3.0 \text{ kcal/mole (Pb}_2\text{O}_2\text{)}$$

$$\Delta H_{1040}^{\circ} = 122.4 \pm 5.0 \quad " \quad (\text{Pb}_3\text{O}_3)$$

$$\Delta H_{1040}^{\circ} = 196.5 \pm 7.0 \quad " \quad (\text{Pb}_4\text{O}_4)$$

By combining these values with the free energy change for the corresponding reaction, the entropies $S_{1040}^{\circ} = 99.4 \pm 4.0$; $S_{1040}^{\circ} = 130.3 \pm 5.0$; $S_{1040}^{\circ} = 156.5 \pm 7.0$ e.u. were calculated for the dimer, trimer and tetramer respectively. By estimating heat contents and entropy variation with temperature by analogy with a number of tetra, hexa and octoatomic molecules⁽²⁷⁾ the polymerization energies and entropies at 298°K were calculated to be

$$\Delta H_{298}^{\circ} = 63.4 \pm 4.0 \text{ kcal/mole (Pb}_2\text{O}_2\text{)}$$

$$\Delta H_{298}^{\circ} = 126.4 \pm 6.0 \quad " \quad (\text{Pb}_3\text{O}_3)$$

$$\Delta H_{298}^{\circ} = 202.0 \pm 10.0 \quad " \quad (\text{Pb}_4\text{O}_4)$$

and $S_{298}^{\circ}(\text{Pb}_2\text{O}_2) = 75.0 \pm 6.0$; $S_{298}^{\circ}(\text{Pb}_3\text{O}_3) = 92.4 \pm 8.0$ and $S_{298}^{\circ}(\text{Pb}_4\text{O}_4) = 106.5 \pm 10.0$ e.u. For Pb_5O_5 and Pb_6O_6 for which no second law value could be obtained for reaction (6), an estimate of S_{1030}° was made by adding 30 and 60 e.u. to the entropy of Pb_4O_4 . With the values $S_{1040}^{\circ}(\text{Pb}_5\text{O}_5) = 187$ e.u. and $S_{1040}^{\circ}(\text{Pb}_6\text{O}_6) = 217$ e.u. and assuming $\Delta S_{1040}^{\circ} = S_{1200}$, the relation $\Delta G_T^{\circ} = \Delta H_T^{\circ} - T\Delta S_T^{\circ}$ leads to

$$\Delta H_{1200}^{\circ} = 253 \pm 20 \text{ kcal/mole (Pb}_5\text{O}_5\text{)}$$

$$\Delta H_{1200}^{\circ} = 320 \pm 30 \text{ kcal/mole (Pb}_6\text{O}_6\text{)}$$

These values were used to draw the dotted lines in fig.1.

TABLE 3. Reinterpretation of Total Pressure Measurements
for PbO.

Authors	Method	Number of points	T (°K)	-log p ^M (atm)	-log(PbO) (atm)	ΔH_{298}^0 (kcal/mole)
Feiser ⁽¹¹⁾	Flow	3	1023	4.58	6.00	68.3
		(below MP)	1073	3.98	5.40	68.5
		7	1123	3.32	4.77	68.4
		7	1173	2.93	4.26	68.5
		(above MP)	1473	1.17	2.10	70.4
Richardson and Webb ⁽¹²⁾	Knudsen	2	1373	2.18	2.82	70.3
			1473	1.70	2.23	71.2
Richards ⁽¹³⁾	Flow	1	1073	4.85	5.66	69.8
Horbe and Knacke ⁽¹⁴⁾	Flow	9	1198	2.95	4.13	69.1
			1500	1.26	2.04	71.1
Nesmayanov, Firsova and Isakova ⁽¹⁵⁻¹⁶⁾	Knudsen	6	1029	4.34	5.81	67.8
			1091	3.78	5.10	68.2
			1106	3.48	4.87	68.8
			1117	3.85	4.89	68.6
			1121	3.98	4.92	69.1
			1151	3.45	4.50	68.6
	Langmuir	15	887	7.01	8.13	68.2
			896	7.07	8.03	68.5
			916	6.88	7.77	68.8
			926	6.64	7.58	68.7
			935	6.09	7.28	68.2
			939	6.37	7.35	68.7
			952	6.17	7.12	68.6
			955	6.72	7.16	69.0
			964	5.98	6.92	68.7
			973	6.09	6.78	68.6
			980	5.67	6.66	68.5
			1014	5.49	6.28	68.9
			1023	5.08	6.10	68.8
			1037	5.04	5.95	68.9
			1043	4.81	5.82	68.7
	Flow	15	1055	4.68	5.76	69.1
			1061	4.90	5.77	69.6
			1065	4.50	5.60	69.0
			1072	4.35	5.50	69.0
			1073	4.21	5.45	68.8
			1075	4.36	5.48	69.1
			1083	4.27	5.40	69.2
			1087	4.20	5.35	69.5
			1095	4.27	5.25	69.1

TABLE 3. Continued

Authors	Method	Number of points	T (°K)	$-\log^M$ (atm)	$-\log(\text{PbO})$ (atm)	ΔH_{298}^0 (kcal/mole)
Nesmeyanov	Flow	15	1101	4.29	5.21	69.2
Firsova and			1107	4.19	5.12	69.2
Isakowa(15-16)			1115	3.97	5.02	69.1
(continued)			1136	3.90	4.82	69.4
			1149	3.67	4.65	69.3
			1153	3.51	4.58	69.1
Knacke and Prescher(10)	Knudsen	37	963	5.72	6.85	68.2
			1063	4.40	5.50	68.4
			1163	3.30	4.36	68.5
	Boiling point	1	1808	0.00	0.42	70.9
average:						68.9

6. DISCUSSION.

a. Reinterpretation of total pressure measurements.

Several authors⁽¹⁰⁻¹⁶⁾ listed in table 3 have measured apparent total pressures above PbO(s) using Knudsen, Langmuir and transport methods and assuming the vapor to contain only the molecule PbO. The partial pressure of PbO can be calculated from these apparent total pressures by taking the presence of the polymers and decomposition products into account by use of the relations:

$$\begin{aligned}
 P_{K,L}^M &= p(\text{Pb})(M_{\text{Pb}}/M_{\text{PbO}})^{1/2} + p(\text{O}_2)(M_{\text{O}_2}/M_{\text{PbO}})^{1/2} + \sum_{n=1}^{n=6} n^{1/2} p(\text{Pb}_n\text{O}_n) \\
 &= p(\text{Pb})(M_{\text{Pb}}^{1/2} + 1/2 M_{\text{O}_2}^{1/2})/M_{\text{PbO}}^{1/2} + \sum_{n=1}^{n=6} n^{1/2} p(\text{PbO})^n/K_n
 \end{aligned}$$

(Knudsen and Langmuir)

$$P_T^M = p(\text{Pb})(M_{\text{Pb}}/M_{\text{PbO}}) + p(\text{O}_2)(M_{\text{O}_2}/M_{\text{PbO}}) + \sum_{n=1}^{n=6} np(\text{Pb}_n\text{O}_n)$$

$$= (K/M_{\text{PbO}} \cdot p(\text{O}_2)^{1/2}) \times (M_{\text{Pb}} + M_{\text{O}_2} \cdot p(\text{O}_2)^{3/2}/K) + \sum_{n=1}^{n=6} np(\text{PbO})^n/K_n$$

where K is the equilibrium constant for reaction 3 and K_n the equilibrium constant for the reactions given in Fig.1. When oxygen at high pressure is used as carrier gas the first term can be neglected. When an inert gas is used as carrier gas, the first term becomes equal to the Pb decomposition pressure since then $p(\text{Pb}) = 2p(\text{O}_2)$.

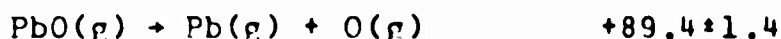
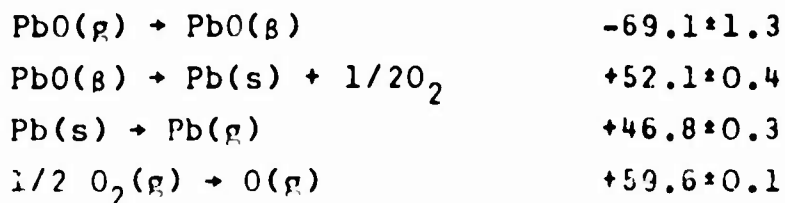
The partial PbO pressure can also be calculated at the boiling point of PbO(s) ⁽¹⁰⁾ by use of the relation:

$$\begin{aligned} 1.00 &= p(\text{Pb}) + p(\text{O}_2) + \sum_{n=1}^{n=6} p(\text{Pb}_n\text{O}_n) \\ &= 3/2 p(\text{Pb}) + \sum_{n=1}^{n=6} p(\text{PbO})^n/K_n \end{aligned}$$

These partial pressures and original apparent total pressures P_T^M are given in table 3 together with the heat of sublimation of the monomer based thereon. The main terms in the correction are due to the presence of Pb_2O_2 and Pb_2O_4 . The average value obtained $\Delta H_{298}^0(\text{sub}, \text{PbO}) = 68.9 \text{ kcal/mole}$ is in excellent agreement with the value measured directly in this work.

b. Dissociation energy of PbO.

The dissociation energy of the molecule PbO was calculated from the cycle:



The value used for the heat of sublimation of lead monoxide is the average of the values of Tables 2 and 3, $\Delta H_{298}^0(\text{PbO}) = 69.1 \pm 1.3$ kcal/mole. Other thermodynamic data were taken from the literature (25,26,27). The value obtained $D_{298}^0(\text{PbO}) = 89.4 \pm 1.4$ kcal/mole leads to $D_0^0(\text{PbO}) = 88.4 \pm 1.4$ kcal/mole or 3.83 ± 0.05 e.V.

The thermochemical value for the dissociation energy can be compared with that obtained by a linear Birge Spomer extrapolation for the vibrational levels of the ground state, $D_0''(\text{PbO}) = 4.3$ e.V. As often, the Birge Spomer extrapolation leads to too high a value.

A cross check can however be found in the spectroscopic data for the excited E state, which most probably correlates with the atoms in their $\text{Pb}(^3\text{P}_1) + \text{O}(^3\text{P}_1)$ sublevels⁽¹⁸⁾. The E state is known⁽¹⁷⁾ up to 4.86 eV above the ground state which is thus a lower limit for the convergence limit. On subtracting the excitation energy of the $\text{Pb}(^3\text{P}_1)$ and $\text{O}(^3\text{P}_1)$ levels, 0.97 and 0.02 eV respectively, the limit gives $D_0''(\text{PbO}) \geq 3.87$ eV. The comparison with the thermochemical value thus suggests that the breaking-off of the vibrational levels in the E state corresponds with the actual limit or is at least very close to it.

c. Polymerization energies.

The lead oxide polymers are quite analogous to those for the other Group IV_B oxides^(1,7,8). It is however interesting to notice that in going from Si to Ge, Sn and Pb the number of polymers detected and their concentration increase regularly.

Both the average PbO-PbO bond in (PbO)_n and the energy required to abstract one PbO from a given polymer show an interesting trend (Table 4) and are quite close to the heat of sublimation of the monomer. The same was previously noted for the other polymers of the Group IV_B-Group VI_B molecules⁽³⁻⁹⁾ and suggests that the gaseous polymers have structures and binding forces closely related to those of the lattice.

TABLE 4. Stability of PbO polymers.

(A) $\text{Pb}_n\text{O}_n(\text{g}) \rightarrow \text{Pb}_{n-1}\text{O}_{n-1}(\text{g}) + \text{PbO}(\text{g})$		
(B) $\text{Pb}_n\text{O}_n(\text{g}) \rightarrow n \text{ PbO}(\text{g})$		
Pb_nO_n	ΔH_{298}°	$1/n \Delta H_{298}^{\circ} (\text{B})$
Pb_2O_2	63.4	63.4
Pb_3O_3	63.0	63.2
Pb_4O_4	75.6	67.3
Pb_5O_5	59.0	65.4
Pb_6O_6	69.0	66.0
$\text{PbO}(\text{s})$	69.1	69.1

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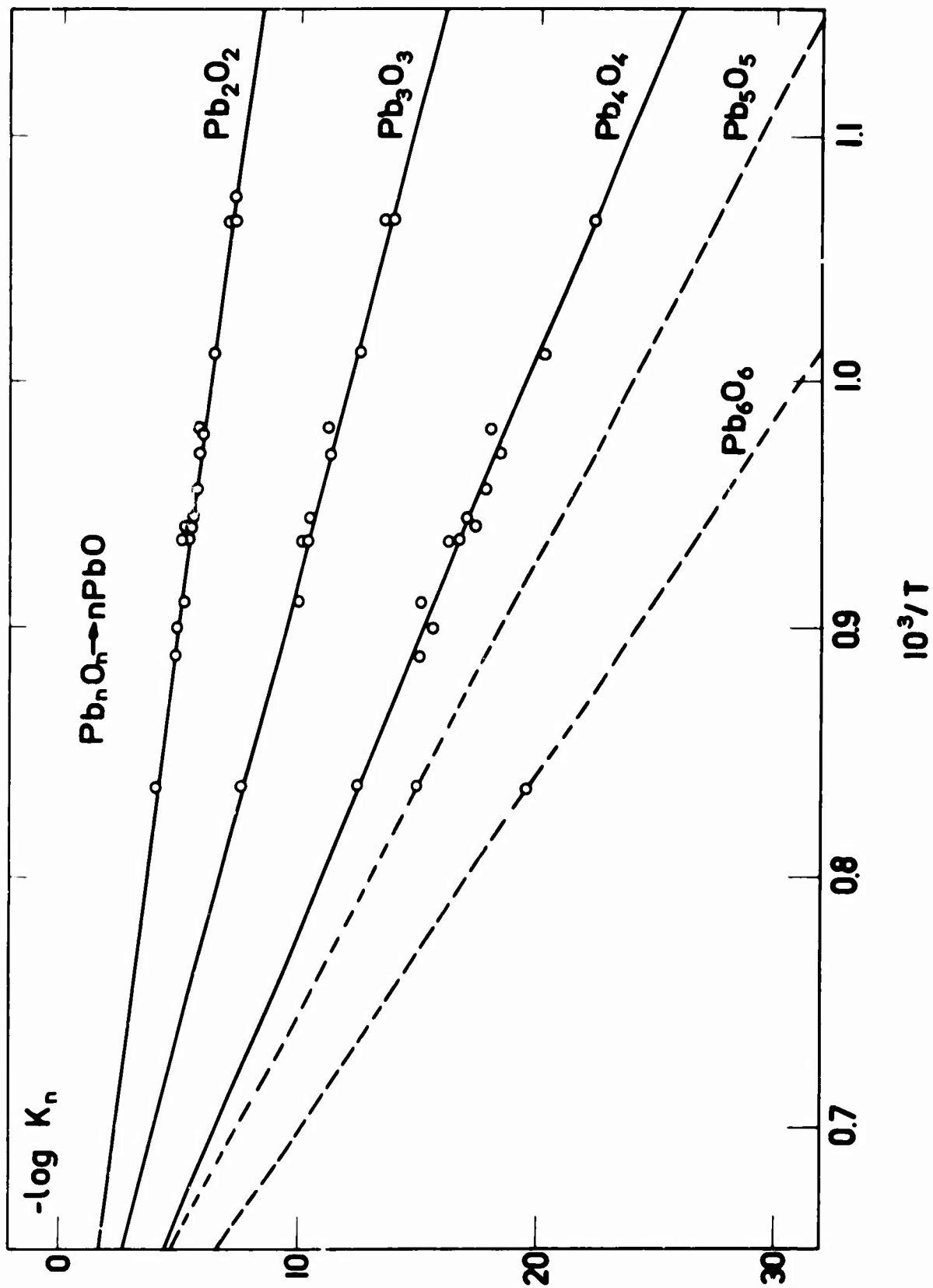


Figure 1. Equilibrium Constants for The Reactions $(PbO)_n \rightarrow n PbO(g)$