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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART XXIII. THERMOCHEMICAL STUDY OF THE GERMANIUM OXIDES USING A MASS SPECTROMETER — THE DISSOCIATION ENERGY OF THE MOLECULE GeO

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NOTICES

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FOREWORD

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ABSTRACT

The mass spectrometric study of the vaporization of the compounds GeO_2(hex) and GeO(am) and of the mixture GeO_2(hex) + Ge(c) made it possible to establish their mode of vaporization:

$$GeO_2(hex) - GeO(g) + 1/2O_2 \quad (I)$$

$$n\ GeO(am) - (GeO)_n(g)\ (n = 1, 2, 3) \quad (II)$$

$$n/2\ GeO_2(hex) + n/2\ Ge(c) - (GeO)_n(g)\ (n = 1, 2, 3) \quad (III)$$

The enthalpies of vaporization are

$$\Delta H^\circ_{298}(I) = 121.2 \pm 1.6 \text{ kcal/mole}$$
$$\Delta H^\circ_{298}(II,\ n = 1) = 53.4 \pm 1.0 \text{ kcal/mole}$$
$$\Delta H^\circ_{298}(III,\ n = 1) = 58.2 \pm 1.0 \text{ kcal/mole}$$

The polymerization energies are

$$\Delta H^\circ_{298}(GeO\text{-}GeO) = 44.7 \pm 3.0 \text{ kcal/mole}$$

$$\Delta H^\circ_{298}(GeO\text{-}GeO\text{-}GeO) = 88.5 \pm 5.0 \text{ kcal/mole}$$

Total pressures given in the literature were reinterpreted taking the presence of the polymers into account.

The heat of formation of the metastable compound GeO (am) obtained here is $\Delta H_f^\circ(\mathrm{GeO}) = -59.6 \pm 0.7$ kcal/mole.

The dissociation energy of the gaseous molecule GeO is $D_0^\circ(\mathrm{GeO}) = 157.4 \pm 1.5$ kcal/mole.

This technical documentary report has been reviewed and is approved.

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INTRODUCTION.

As part of a study[1] of the composition of the vapors in equilibrium with the group IVB-Group VIB compounds and of the thermochemical determination[2] of the dissociation energy of the corresponding molecules and of their polymers, the vapor over germanium monoxide, a mixture of germanium dioxide + germanium[3] and germanium dioxide[3] was analyzed mass spectrometrically.

Germanium monoxide is metastable and disproportionates to germanium and germanium dioxide[4,5]. Details concerning this disproportionation were obtained in the present study.

Germanium dioxide can exist in three modifications, the quadratic, hexagonal and glassy[6]. Although the low temperature form is the quadratic (insoluble) form, the more common one is the hexagonal (soluble) form. The heat of formation[7] and thermodynamic properties of the hexagonal form are accurately known[8]. To the extent to which similar glassy GeO_2 samples can be obtained, the thermodynamic properties of the latter are also established[8].

The total pressures of the mixture of hexagonal GeO_2 and cristalline germanium and of the metastable compound GeO were determined by Bues and von Wartenberg[4] and by Jolly and Latimer[5]. The former authors measured the pressure of both systems by a manometric method and that of GeO_2(hex) + Ge(c) also by the transport method. The latter authors applied the Knudsen technique to initial GeO samples but concluded that these had disproportionated to GeO_2 + Ge. From their own measurements and from those of Bues and von Wartenberg, Jolly and Latimer deduced the dissociation energy of the GeO molecule, D_0^o(GeO)= 157.2±3.0 kcal/mole, compared to the value D_0^o(GeO) = 157±4 kcal/mole estimated by analogy with SiO from spectroscopic data by Barrow and Rowlinson[9]. From the data of Bues and von

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Wartenberg for GeO and for GeO_2 + Ge, Jolly and Latimer also deduced an approximate heat of dismutation of GeO of about -7 kcal/mole.

The pressure of GeO_2, contained in quartz cells, was determined by Davidov[(10)], using the Knudsen technique and with the assumption that the gaseous molecule is GeO_2 (or a polymer thereof). Shchukarev and Semenov[(11)] studied the sublimation of the same substance mass spectrometrically and identified the molecules $(GeO)_2$ and $(GeO)_3$.

The systematic mass spectrometric study[(1-2)] of the sublimation of the Group IVB-Group VIB compounds (Group IVB= C, Si, Ge, Sn, Pb represented by Me; Group VIB= O, S, Se and Te represented by X) as well as the previous mass spectrometric study of SiO_2 and SiO_2 + Si by Porter, Chupka and Inghram[(12)] indicated that the polymers $(MeX)_n$ are typical of the MeX compounds or MeX_2 + Me mixtures, but not of the MeX_2 compounds, which vaporize predominently by one of the two processes $MeX_2(s) \rightarrow MeX(s) + 1/2X_2(g)$ or $MeX_2(s) \rightarrow MeX(g) + 1/2X_2(g)$.

The sublimation of GeO(s), of the mixture GeO_2(hex)+ Ge(c) and of GeO_2(hex) was therefore reinvestigated.

The present paper reports the results of these studies which made it possible to explain and reconcile the pressure data in the literature, to obtain independant values for the heat of formation of the metastable compound GeO and for the free energy of glassy relative to hexagonal germanium dioxide. It further made it possible to determine the thermodynamic properties of gaseous Ge_2O_2 and Ge_3O_3. The thermochemical data for the dissociation energy of GeO are also discussed.

EXPERIMENTAL TECHNIQUE.

The experimental technique and procedure have been described in detail earlier[13]. The mass spectrometer used [14,15] is a single focussing, 20cm radius of curvature, 60° sector instrument, equipped with a secondary electron multiplier[16]. The Knudsen cells containing the samples were made out of quartz and were placed within molybdenum shells heated by radiation from a concentric tungsten loop. The temperatures were measured with Pt-Pt 10% Rh thermocouples. The dimensions of the almost circular effusion orifices were measured with a microcomparator. Their area was varied between 5×10^{-3} and $10^{-2} cm^2$ and was small compared to the surface of the sample. The thickness of the effusion orifice was also measured to evaluate the Clausing[17] factor (about 0.8). The samples were standard germanium (99.999% purity) and hexagonal germanium dioxide (checked by X ray examination). The metastable monoxide was prepared by vacuum sublimation of a stoechiometric GeO(hex) + Ge mixture, as described by Bues and von Wartenberg[4]. It was brown-black and amorphous as verified by X ray examination.

RESULTS

1. <u>Composition of the Vapor and Pressures.</u>

The ions formed by electron impact from the molecular beam issuing from the cell containing either GeO(am) or GeO_2(hex) + Ge(c) are Ge^+, GeO^+, Ge_2O^+; $Ge_2O_2^+$ and $Ge_3O_3^+$. These formed from cells containing GeO_2(hex) are O_2^+, Ge^+ and GeO^+. The approximate appearance potentials were obtained by the linear extrapolation method, the energy scale being calibrated with the appearance potentials of the H_2O^+ ion[18].

They are Ge^+, 14.0±1, GeO^+, 10.1±0.8, O_2^+, 12.2±0.5, Ge_2O^+, 14.3±1.0, $Ge_2O_2^+$, 8.7±1.0 and $Ge_3O_3^+$, 8.6±1.0 eV.

The appearance potential of GeO^+, 10.1±0.8 eV compared to that of a number of isoelectronic ions, N_2^+, 15.6[18], P_2^+, 10±0.5[19](11.8±0.5)[20], As_2^+, 10±0.5[21] (11.0±0.5)[20], Sb_2^+, 8.4±0.3[22], CO^+, 14.0[18], SiO^+, 10.5[9](10.8±0.5)[12] and SnO^+, 10.0±0.7[2], indicates this ion to be formed directly from the GeO molecule. Similarly, the appearance potentials of the ions $Ge_2O_2^+$, 8.7±1 eV and Ge_3O_3, 8.6±1 eV indicate these to be parent ions from the corresponding molecules. The appearance potential of the ion Ge^+, 14.0±1 eV compared to the spectroscopic value for the ionization potential, 8.13 eV[23] shows this ion to be formed by fragmentation, mainly of the GeO molecule.The situation is analogous for Ge_2O^+, whose appearance potential is much higher than expected for a parent ion. It is considered to be formed by fragmentation, mainly of the Ge_2O_2 molecule. The predominant molecules in the vapors of both the GeO(am) and GeO_2(hex) + Ge systems are therefore GeO, Ge_2O_2 and Ge_3O_3. In the GeO_2 system, they are GeO and O_2.

The main vaporization processes are thus:

$$nGeO(am) \rightarrow (GeO)_n(g) \qquad n = 1,2,3$$

$$\frac{n}{2}\,GeO_2(hex) + \frac{n}{2}\,Ge(c) \rightarrow (GeO)_n(g) \quad n=1,2,3$$

$$GeO_2(hex) \rightarrow GeO(g) + 1/2O_2(g)$$

The partial pressures were determined either by completely subliming samples of a few mg or by determining the weight lost by sublimation during a given time by more important samples. In both cases, the different $(GeO)_n^+$ intensities were measured and integrated with time. By replacing in the Hertz-Knudsen relation, $G = P(M/2\pi RT)^{1/2} st$ (G= weight loss, P= pressure, M= molecular weight of the subliming molecule, R= gas constant, T= temperature, s= effective area of the effusion orifice, t= interval at temperature T) the pressure by $p_n = I_n T/\sigma_n \gamma_n k$ (I_n= intensity of species n, σ_n= relative ionization cross section of species n, γ_n= secondary electron multiplier yield for ion n, k= proportionality constant), one obtains, when several species r are simultaneously responsible for the weight loss and when the experiment is carried out at several successive temperatures during a given time interval t

$$G = \frac{s}{\sigma_1 \gamma_1 k}\left(\frac{M}{2\pi R}\right)^{1/2} A_1 \left\{ 1 + \Sigma\, n^{1/2} \frac{A_n \sigma_1 \gamma_1}{A_1 \sigma_n \gamma_n} \right.$$

with $A_n = \Sigma I_n T^{1/2} \Delta t$

By analogy with a number of diatomic[24] and dimeric[25] molecules, the ratio $\sigma_{Ge_2O_2}/\sigma_{GeO}$ was taken equal to 1.6. The ratio $\sigma_{Ge_3O_3}/\sigma_{GeO}$ was taken equal to 2.1. The relative multiplier yields were read from the calibration curve of the multiplier[26]. Molecular effects were corrected for as suggested by Stanton, Chupka and Inghram[27]. The numeric values used are 1, 0.61 and 0.52 for GeO, Ge_2O_2 and Ge_3O_3 respectively.

The partial pressures are given separately for GeO(am), GeO_2(gl) + Ge(c) and GeO_2(hex) + Ge(c) in figures 1-3.

2. Disproportionation of Germanium Monoxide.

As expected for a metastable system, the pressure (intensity) of the different gaseous species in equilibrium with GeO were higher than those for the GeO_2(hex) + Ge(c) mixture at the same temperature. (This feature made it possible to study the $(GeO)_n$(g) → nGeO(g) (n=2,3) equilibria over a much wider temperature interval than would have been the case in the GeO_2(hex) + Ge(c) system alone).

When increasing the temperature to about 800°K, the intensity (pressure) of all three $(GeO)_n$ species decreased with time and temperature and eventually reached a new steady level, indicating disproportion to have occured. In four experiments, carried out with samples of comparable size (100mg) the temperatures at which the disproportionation took place was the same within some 25°. The apparent rate of transformation which was not studied systematically was also rather reproducible.

After disproportionation the partial pressure of the three $(GeO)_n$ species were however still about 3^n times higher than those in the GeO_2(hex) + Ge(c) system. It was therefore concluded that the GeO_2 formed was not the hexagonal but the glassy form. X ray examination of a sample obtained by interrupting one experiment immediately after the disproportionation took place showed only the presence of cristalline germanium. Another argument for considering the GeO_2 formed to be glassy form is that the GeO partial pressure as well as its temperature dependence within the interval 770-830°K was not entirely reproducible from one experiment to the other, indicating slightly different "glasses" to be formed. It is further to be noted that the slope dlnP/d1/T was in one experiment higher rather than lower than that for the GeO_2(hex) + Ge(c) system, which is a thermodynamic inconsistency.

When the samples of GeO_2(glassy) + Ge(c) obtained by disproportionation of amorphous GeO were heated to about 900°K, a further decrease in partial pressures gradually took place. The relative intensities of the $(GeO)_n$ species and the absolute pressures became identical with those in the GeO_2(hex)+Ge(c) system. X ray examination of the samples so obtained now showed the presence of hexagonal GeO_2 in addition to the cristalline germanium. The observations presented for clarity for GeO(g) alone, are represented in figure 4. The disproportionation of GeO to glassy GeO_2 + Ge and the transformation of glassy into hexagonal GeO_2 are in agreement with Ostwald's rule.

In an attempt to observe also the transformation of hexagonal into quadratic dioxide, a mixture of the former and of cristalline germanium was heated up to 1000°K. No transformation took place under the conditions of the experiment. Because of the value of the pressures at the latter temperature, which are at the limit where Knudsen conditions are still satisfied, the sample was not heated to higher temperatures.

3. Entropy and Stability of Gaseous Ge_2O_2 and Ge_3O_3.

The relatively large interval accessible and the ratios of intensity (pressures) made it possible to determine both the entropy and the stability of gaseous Ge_2O_2 and Ge_3O_3 by a second law treatment (figure 5). A least square calculation gave ΔH^o_{850}= 43.0±0.75 kcal/mole and ΔS^o_{850}= 30.2±0.9 e.u. for the reaction Ge_2O_2(g) → 2GeO(g) and ΔH^o_{850}= 85.1±2.0 kcal/mole and ΔS^o_{850}= 57.0±2.4 e.u. for Ge_3O_3(g) → 3GeO(g). The error limits are statistical errors. An estimate of the heat content by analogy with other tetratomic and hexatomic molecules then gave ΔH^o_{298}(dim)= 44.7±3.0 kcal/mole and ΔH^o_{298}(trim)=88.5±5 kcal/mole, the error limits now being estimated over all uncertainties. The entropies of Ge_2O_2 and Ge_3O_3 obtained from the above entropy changes and the entropy of gaseous GeO[28] are $S^o_{850}(Ge_2O_2)$ =94.6±2,$S^o_{850}(Ge_3O_3)$=130.2±4,$S^o_{298}(Ge_2O_2)$=75.1±3 e.u. and $S^o_{298}(Ge_3O_3)$ = 99.3±5 e.u.

DISCUSSION

Reaction enthalpies ΔH^{o}_{298} were calculated using the relation

$$\Delta G^{o} = -RT\ln K = RT\ln \pi P_{n}^{\nu_{n}} = \Delta H^{o}_{298} + T\Delta\left((G^{o}-H^{o}_{298})/T\right)$$

(ΔG^{o}= change in Gibbs free energy accompanying the reaction considered; K= the equilibrium constant; p_n= the partial pressure, in atm, of the molecule n; ν_n= the stoechiometric coefficient of molecule n; $(G^{o}-H^{o}_{298})/T$= the free energy function).

The numerical values for the free energy functions of Ge(c), GeO(am), GeO(g), GeO_2(gl) and GeO_2(hex) were taken from the literature as referred to (TABLE I).

1. Thermodynamic properties of the condensed compounds.

a. Heat of formation of germanium monoxide.

The ratio of the GeO pressures over the metastable monoxide and over the mixture of GeO_2(hex)+Ge(c) (figure 4) directly gives the free energy of dismutation. Since the ratio of pressures or more precisely, intensities, was obtained each time within one single experiment and was therefore independent of instrumental factors, the accuracy is quite good.

The average value at 800°K is ΔG^{o}_{800}= -4.1±0.3 kcal/mole.

Together with the free energy function estimated by Coughlin[30] it gives ΔH^{o}_{298}= -5.3±0.6 kcal/mole. It can be compared with the ΔH^{o}_{298} value derived for the same reaction, viz. GeO(s) → 1/2GeO_2(hex) + 1/2Ge(c) determinated by e.m.f. measurements by Jolly and Latimer[31] for the GeO/GeO_2 couple:

$$GeO(s)+H_2O(1) \rightarrow GeO(hex)+2H^+ +2e \qquad E=0.118\pm0.010 \text{ mV}$$
$$\text{or } \Delta G^o_{298}=-5.442\pm0.46 \text{ kcal/mole} \quad (31)$$

$$2H^+ + 2e \rightarrow H_2(g) \qquad \Delta G^o_{298} = 0 \text{(standard electrode)}$$
$$H_2(g)+1/2O_2(g) \rightarrow H_2O(1) \qquad \Delta G^o_{298}=-56.690\pm0.001 \text{ kcal/mole} \quad (32)$$
$$1/2GeO_2(hex) \rightarrow 1/2Ge(c)+1/2O_2(g) \qquad \Delta G^o_{298}=+58.095\pm0.200 \text{ kcal/mole} \quad (8)$$

$$GeO(s) \rightarrow 1/2GeO_2(hex)+1/2Ge(c) \qquad \Delta G^o_{298}=-4.037\pm0.5 \text{ kcal/mole}$$

leading to $\Delta H^o_{298}= -4.5\pm0.5$ kcal/mole.
The two figures are in agreement but the magnitude of the uncertainties in the ΔG measurements does not warrant an estimate of both ΔH^o and ΔS^o from the temperature variation of ΔG^o.

Together with the heat of formation of GeO_2(hex)[8], $\Delta H^o_{298,f}= -129.080\pm0.13$ kcal/mole, the average of the above values for $\Delta H^o_{298}= -4.9\pm0.6$ kcal/mole values leads to the heat of formation of amorphous GeO, $\Delta H^o_{298,f}= -59.6\pm0.7$ kcal/mole.

b. Free energy of transformation of glassy into hexagonal germanium dioxide.

The free energy of transformation of glassy into hexagonal germanium dioxide was obtained from the pressure ratio in the same way as the heat of dismutation of the monoxide. The average value is $\Delta G_{800}= -2.3\pm0.8$ kcal/mole, compared to the figure -1.5 kcal listed by Mah and Adami[7] for one particular glass sample. If meaningful, the difference indicates the glasses not to be identical. Since the present data do not permit to separate enthalpy and entropy contributions, the thermodynamic data given for glassy GeO_2 by Adami and Mah were used in the subsequent calculations.

2. Heat of sublimation of GeO;

The heats of sublimation of GeO from amorphous GeO, from the mixture of glassy GeO_2+cristalline Ge and from the mixture of hexagonal GeO_2+cristalline Ge are summarized in table 2-4.

3. Reinterpretation of Total Pressures.

a. Germanium Monoxide.

The pressures over samples which were initially metastable GeO, determined by Bues and von Wartenberg, were measured by a manometric method and are therefore the sum of the partial pressure of the monomer, dimer and trimer, provided those of higher polymers not observed here can be neglected. The total pressure given by the latter authors were reinterpreted accordingly, using the extrapolated equilibrium constants for the reactions $(GeO)_n(g) \rightarrow n(GeO)(n=2,3)$(see fig.5). The partial GeO pressures so obtained are represented in Fig.6 which summarizes the data for the different systems and investigations.

The pressures measured by Jolly and Latimer for initial GeO samples by the Knudsen method can be reinterpreted in a similar way, writing

$$P^{*}_{GeO} = P_{GeO}(1+\sqrt{2}\ \frac{P_{Ge_2O_2}}{P_{GeO}} + \sqrt{3}\ \frac{P_{Ge_3O_3}}{P_{GeO}})$$

where P^{*}_{GeO} is the apparent GeO pressure.

The pressure measurements by the latter authors were carried out in the temperature region were in the present experiments disproportionation occured. The apparent scatter in the points obtained by the authors referred to indicates that the same probably occured during their experiments. Of the eight measurements, numbered here (Table 5) 1-8 in the sequence in the original publication[5], three (n°1,2,4) were carried out with fresh samples[33]. The pressure in run 1 is quite close to those obtained here before disproportionation occured and probably corresponded to GeO(am). The pressures in runs 2 and 4 are close but somewhat above those for $Ge+GeO_2(gl)$, probably indicating that <u>during</u> the measurement disproportionation occured. The corresponding pressures are therefore considered to represent upper limits for the system $Ge(c)+GeO_2(gl)$. The pressures for runs 3, 5, 6 and 7 are in good agreement with these measured here for $Ge(c)+GeO_2(gl)$ and are therefore considered to pertain to that system and to confirm the present values. The pressure in run 8 finally was obtained at a temperature at which $GeO_2(gl)$ had transformed in the present work into $GeO_2(hex)$. The same probably occured during the measurement by Jolly and Latimer which therefore gives an upper limit for the $Ge(c)+GeO_2(hex)$ system.

Since in this temperature range, the di and trimer are relatively unimportant, the total pressure is close to the partial pressure of the monomer. Therefore, the Knudsen measurements by Jolly and Latimer are a cross check of the present measurements, which depend on the estimate of the relative ionization cross sections.

b. $GeO_2(hex) + Ge(c)$.

The total pressures by Bues and von Wartenberg, measured by a manometric and by the transport method were reinterpreted in a similar manner as explained above, but taking into account that in the transport method

$$P^{*}_{GeO} = P_{GeO}\left(1 + 2\frac{P_{Ge_2O_2}}{P_{GeO}} + 3\frac{P_{Ge_3O_3}}{P_{GeO}}\right)$$

The partial GeO pressures obtained and the heat of vaporization of GeO calculated therefrom are summarized in table 6 and fig.6.

c. $\underline{GeO_2}$

The pressures measured by Davydov[10] by the Knudsen method and calculated under the assumption that the gaseous molecule is GeO_2 were recalculated to take the stoechiometry of reaction 3 into account. The relation between the apparent pressures is

$$P_{GeO} = P^{*} \left(\frac{M_{GeO_2}}{M_{GeO}}\right)^{1/2} \left(\frac{1}{1+(M_{O_2}/2M_{GeO})}\right)$$

The recalculated partial GeO and O_2 pressures are given in table 7 together with the enthalpy for reaction 3. The results show a marked variation. Davydov attributed this to the transformation of hexagonal into quadratic GeO_2. The reaction enthalpy for the first two points at 1159 and 1201°K corresponds to the value calculated from the dissociation energy of GeO and the heat of formation of hexagonal GeO_2. It is therefore accepted that these points indeed correspond to the vaporization of hexagonal GeO_2. The last two or three points should also correspond to hexagonal GeO_2 since the quadratic form becomes unstable relative to the preceding one at 1306±10°K[6]. Even if the transition did not occur the use of the thermodynamic functions of one form for the other should for these points not introduce a serious difference in ΔH. It is threrefore suggested that the difference between Davydov's first two points and the others (omitting the third), 5.1 kcal/mole corresponds to the partial heat of mixing of GeO_2 in SiO_2. It may be noted that Davydov observed an interaction between GeO_2 and SiO_2 which was also noticed here when GeO_2 was vaporized from SiO_2 crucibles.

The observation of the Ge_2O_2 and Ge_3O_3 polymers in the vaporization of GeO_2 by Shchukarev and Semenov[11] is completely at variance with the mass spectrometric and thermodynamic results of the present study. In the investigation referred to, GeO_2 was vaporized from a platinum filament attached to a nichrome holder. A plausible reason of the discrepancy is therefore that GeO_2 was reduced by the latter alloy, which would explain the presence of the polymers, characteristic of the $Ge + GeO_2$ system.

4. Dissociation Energy of the GeO Molecule.

The dissociation energy of the molecule GeO can be calculated from thermochemical cycles based on the heat of sublimation of GeO from amorphous GeO, from the mixture of glassy or hexagonal GeO_2+cristalline germanium and on the heat of formation of hexagonal GeO_2. The values used in completing the cycles are: $D^o_{298}(O_2) = 119.2 \pm 0.1$[34]; $\Delta H^o_{298,s}(Ge) = 89.5 \pm 0.5$; $\Delta H^o_{298,f}(GeO_2, hex) = -129.1 \pm 0.1$[7]; $\Delta H^o_{298,f}(GeO_2, gl) = -125.8 \pm 0.5$[8]; $\Delta H^o_{298,f}(GeO) = -59.6 \pm 0.7$ kcal/mole.

The values obtained in this work and from the reinterpreted literature data are summarized in table 8.

The average is $D^o_{298}(GeO) = 156.1 \pm 1.5$ or $D^o_o(GeO) = 157.4 \pm 1.5$ kcal/mole (6.825 ± 0.06 eV).

REFERENCES.

1. R. Colin and J. Drowart, J.Chem.Phys., 37, 1120 (1962); J.Phys.Chem., 68, 428 (1964); Trans. Faraday Soc., 60, 673 (1964); Technical Note n°10, Contract AF61(052)-225, 28 Feb. 1963.

2. J. Drowart and R. Colin, Technical Note n°15, Contract AF61(052)-225, 15 July 1963.

3. F. Degrève, Ind.Chim.Belg., 28, 752 (1963).

4. W. Bues and H. von Wartenberg, Z.anorg.allgem.Chem., 266, 281 (1951).

5. W.L. Jolly and W.M. Latimer, J.Am.Chem.Soc., 74, 5757 (1952).

6. A.W. Laubengayer and D.S. Morton, J.Am.Chem.Soc., 54, 2303 (1932).

7. A.D. Mah and L.H. Adami, U.S. Bur.Mines R.I. 6034 (1962).

8. K.K. Kelley and A.U. Christensen, U.S. Bur.Mines R.I.5710 (1961)

9. R.F. Barrow and H.C. Rowlinson, Proc.Roy.Soc., A224, 374 (1954).

10. V.I. Davydov, Zhur.Neorg.Khim., 2, 1460 (1957).

11. S.A. Shchukarev and S.A. Semenov, Doklady Akad.Nauk.SSSR, 120, 1059 (1958).

12. R.F. Porter, W.A. Chupka and M.G. Inghram, J.Chem.Phys., 23, 216 (1955).

13. M.G. Inghram and J. Drowart, "Proceedings of a symposium on High Temperature Technology", p.219, McGraw Hill Book Co., New York (1960).

14. J. Drowart and R.E. Honig, J.Chem.Phys., 25, 581 (1956); J.Phys.Chem., 61, 980 (1957).

15. J. Drowart and P. Goldfinger, J.Chim.Phys., 55, 721 (1958).

16. M. Ackerman, F.E. Stafford and J. Drowart, J.Chem.Phys.,33, 1784 (1960).

17. P. Clausing, Z. Physik., 66, 471 (1930).

18. F.H. Field and J.L. Franklin, "Electron Impact Phenomena", Academic Press Inc., N.Y. (1957).

19. J.D. Carette and L. Kervin, Can.J.Phys., 31, 1300 (1961).

20. H. Gutbier, Z.Naturforsch., 16a, 268 (1961).

21. J.S. Kane and J.H. Reynolds, J.Chem.Phys., 25, 342 (1956).

22. G. DeMaria, J. Drowart and M.G. Inghram, J.Chem.Phys., 31, 1076 (1959).

23. C.E. Moore, Natl.Bur.Standards, Circ.n°467 (1949).

24. R. Colin, Ind.Chim.Belg., 26, 51 (1961); M. Jeunehomme, Thesis, Université Libre de Bruxelles (1962); W.L. Fite and R.T. Brackman Phys.Rev., 118, 1141 (1958).

25. J. Berkowitz, H.A. Tasman and W.A. Chupka, J.Chem.Phys., 30, 2170 (1962).

26. M. Ackerman, Thesis, Université Libre de Bruxelles (1960).

27. H. Stanton, W.A. Chupka and M.G. Inghram, Rev.Sci.Instr., 27, 109 (1956).

28. K.K. Kelley, U.S. Bur.Mines Bull.n°584 (1960); K.K. Kelley and E.G. King, U.S. Bur.Mines Bull.n°592 (1961).

29. D.R. Stull and G.C. Sinke, Adv.Chem.Ser. n°18 (1956).

30. J.P. Coughlin, U.S. Bur.Mines Bull. n°542 (1954).

31. W.L. Jolly and W.M. Latimer, J.Am.Chem.Soc., 74, 5751 (1952).

32. F.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine and I. Jaffe, Nat.Bur.Stand., circ. 500 (1952).

33. W.L. Jolly, private communication.

TABLE 1. Free energy functions $-(G^o_T - H^o_{298})/T$ in cal.deg^{-1}·mole^{-1}

T°K	700	800	900	1000	1100
O_2(g)	51.04	51.64	52.22	52.78	53.31
Ge(s)	9.09	9.58	10.06	10.51	10.95
GeO_2(hex)	17.12	18.33	19.51	20.66	21.74
GeO_2(gl)	19.37	20.62	21.79	22.95	24.05
GeO(s)	14.6	15.5	16.3	17.2	18.1
GeO(g)	56.26	56.81	57.42	58.01	58.54

TABLE 2. Heat of sublimation of the molecule GeO from amorphous GeO

T ($^\circ$K)	$-\log p(GeO)$	$-\Delta\left(\frac{G^o_T - H^o_{298}}{T}\right)$ (cal.degree^{-1}.mole^{-1})	ΔH^o_{298} (kcal.mole^{-1})
754	6.46($\pm$0.15)	41.5($\pm$0.6)	53.6
768	6.17	41.4	53.5
775	5.94	41.4	53.2
788	5.76	41.3	53.4
766	6.22	41.4	53.5
757	6.43	41.4	53.6
744	6.73	41.5	53.7
769	6.12	41.4	53.4
778	5.90	41.4	53.2
786	5.79	41.3	53.3
		average	53.4
		statistical error	$\pm$0.2
		total uncertainty	$\pm$1.0

TABLE 3. Heat of sublimation of the GeO molecule from glassy GeO_2 + cristalline germanium.

T (°K)	-log p (atm)	$-\Delta(G^o_T - H^o_{298}/T)$ (cal.degree^{-1} mole^{-1})	ΔH^o_{298} (kcal.mole^{-1})
806	5.66(±0.15)	42.2(±0.5)	54.9
817	5.57	42.2	55.3
843	5.13	42.1	55.3
855	4.97	42.1	55.4
878	4.64	42.1	55.7
789	5.76	42.3	54.1
768	6.54	42.3	54.5
789	6.10	42.3	55.4
800	5.87	42.2	55.3
807	5.77	42.2	55.4
819	5.60	42.2	55.5
830	5.42	42.2	55.6
839	5.31	42.2	55.8
845	5.20	42.2	55.7
844	4.96	42.2	54.7
841	5.05	42.1	54.9
813	5.80	42.2	55.9
769	6.92	42.3	56.9
801	6.04	42.2	55.2
779	6.55	42.3	56.3
770	6.82	42.3	56.6
782	6.48	42.3	56.2
793	6.19	42.3	56.0
818	5.46	42.2	54.9
785	6.47	42.3	56.4
826	5.36	42.2	55.1
		average:	55.0
		statistical error:	±0.8
		total uncertainty:	±1.0

TABLE 4. Heat of sublimation of the GeO molecule from hexagonal GeO_2 + cristalline germanium.

T (°K)	$-\log p_{GeO}$ (atm)	$-\Delta\left(\frac{G^o_T - H^o_{298}}{T}\right)$ (cal.degree.$^{-1}$mole^{-1})	Δ^o_{298} (kcal.mole^{-1})
825	6.20(±0.15)	42.8(±0.4)	58.7
784	6.97	42.9	58.6
770	7.17	42.9	58.3
754	7.72	42.9	59.0
795	6.82	42.9	58.9
840	5.85	42.8	58.4
806	6.56	42.8	58.7
849	5.63	42.7	57.2
880	4.99	42.7	57.6
863	5.35	42.7	58.0
811	6.44	42.8	58.6
779	7.12	42.9	58.8
827	6.19	42.8	58.8
831	6.14	42.8	58.9
851	5.70	42.7	58.6
857	5.59	42.7	58.5
870	5.29	42.7	58.2
882	5.01	42.7	57.9
897	4.68	42.6	57.5
915	4.36	42.6	57.2
937	4.06	42.6	57.3
927	4.20	42.6	57.3
948	3.94	42.5	57.4
		average:	58.2
		statistical error:	±0.7
		total uncertainty:	±1.0

TABLE 5. Reinterpreted pressure data for GeO(am), GeO_2(gl) + Ge(c) and GeO_2(hex) + Ge(c). (Jolly and Latimer - Knudsen technique).

N°	T (°K)	$-\log p^{*}$ (atm)	$-\log p_{GeO}$ (atm)	condensed phase	$-\Delta((G^{o}-H^{o}_{298})/T)$ (cal.degree^{-1}.mole^{-1})	ΔH^{o}_{298} (kcal.mole^{-1})
1	770	5.89	6.30	GeO(am)	41.4	54.0
2	788	5.75	6.08	intermediate	-	-
3	816	5.59	5.78	GeO_2(gl)+Ge(c)	41.7	55.5
4	835	4.96	5.29	intermediate	-	-
5	758	7.17	7.23	GeO_2(gl)+Ge(c)	41.8	56.8
6	816	5.82	5.95	"	41.7	56.2
7	790	6.43	6.51	"	41.7	56.4
8	859	5.11	5.25	GeO_2(hex)+Ge(c)	42.7	57.3

TABLE 6a. Reinterpreted pressure data for GeO(am)
(Bues and von Wartenberg - manometric method).

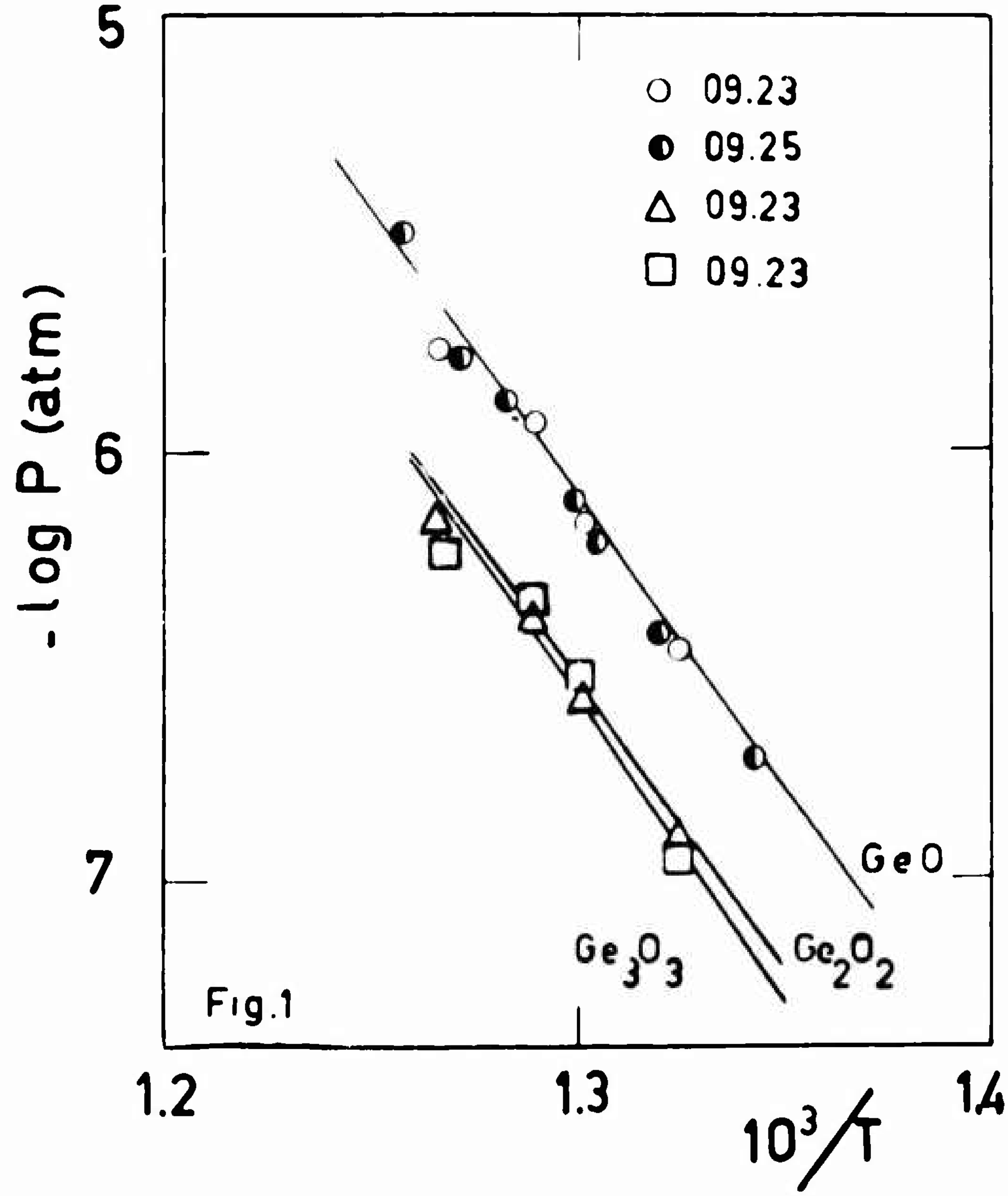
T (°K)	$-\log p^{*}$ (atm)	$-\log p_{GeO}$ (atm)	$-\Delta((G^{o}-H^{o}_{298})/T)$ (cal.degree^{-1}.mole^{-1})	ΔH^{o}_{298} (kcal.mole^{-1})
915	2.63	3.67	41.1	53.0
917	2.36	3.55	41.1	52.6
948	1.89	3.13	40.9	52.4
978	1.43	2.73	40.8	51.1
			average:	52.3

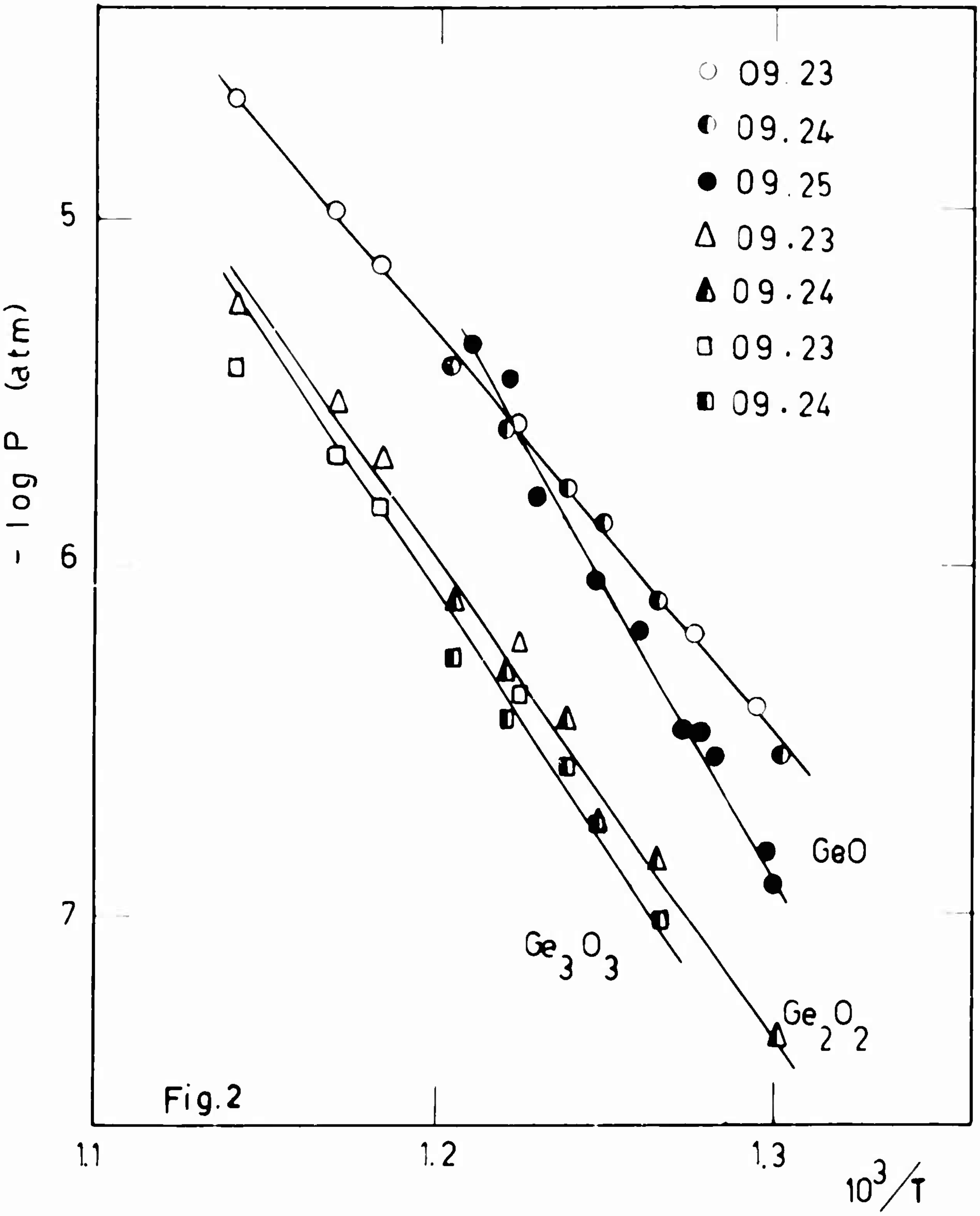
TABLE 6b. Reinterpreted pressure data for GeO_2(hex) + Ge(c)
(Bues and von Wartenberg -manometric and transport methods).

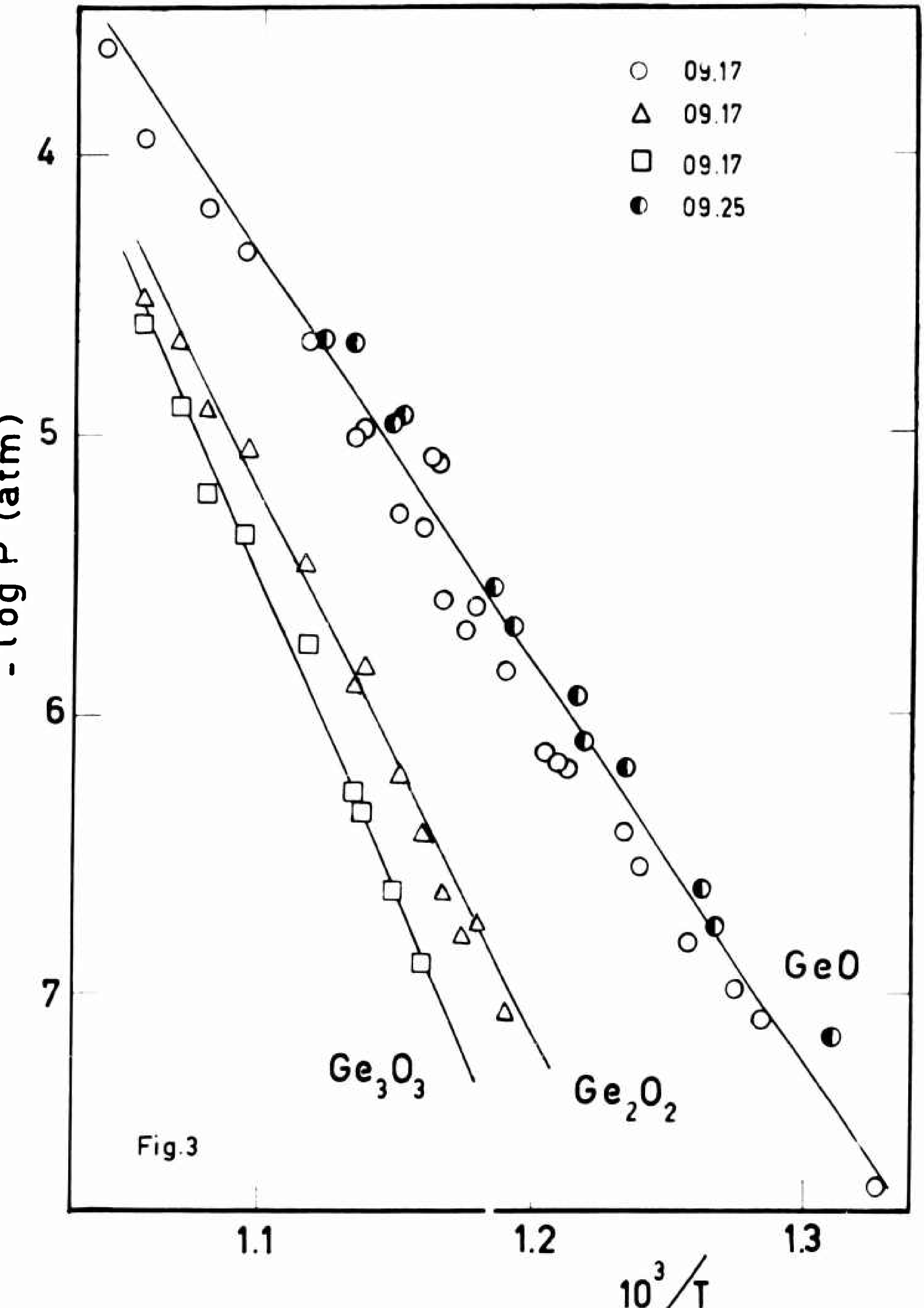
T (°K)	method	$-\log p^{*}$ (atm)	$-\log p_{GeO}$ (atm)	$-\Delta((G^{o}-H^{o}_{298}/T))$ (cal.degree^{-1}.mole^{-1})	ΔH^{o}_{298} (kcal.mole^{-1})
1027	manometric	2.63	3.02	42.4	57.7
1038		2.36	2.95	42.4	58.0
1042		2.62	2.83	42.3	57.6
1057		2.16	2.65	42.3	57.6
1084		1.89	2.40	42.3	57.8
1123		1.43	2.01	42.2	57.7
980	transport	3.05	3.47	42.5	57.2
1081		1.90	2.41	42.3	57.6
				average	57.7

TABLE 7. Reinterpreted pressure data for GeO_2
(Davydov-Knudsen technique)

T (°K)	$-\log p^{*}$ (atm)	$-\log p_{GeO}$ (atm)	$-\log p_{O_2}$ (atm)	$-\Delta((G^{\circ}-H^{\circ}_{298}/T))$ (cal.degree^{-1}.mole^{-1})	ΔH°_{298} (kcal.mole^{-1})
1159	5.62	5.66	6.18	63.3	119.8
1201	5.43	5.47	5.99	63.2	122.5
1227	5.31	5.17	5.69	63.2	124.0
1248	5.23	5.26	5.78	63.1	125.2
1268	5.13	5.17	5.69	63.0	126.4
1288	4.98	5.02	5.54	63.0	127.0
1296	4.75	4.79	5.31	62.9	125.6
1338	4.43	4.46	4.98	62.8	126.7
1351	4.28	4.32	4.84	62.8	126.6

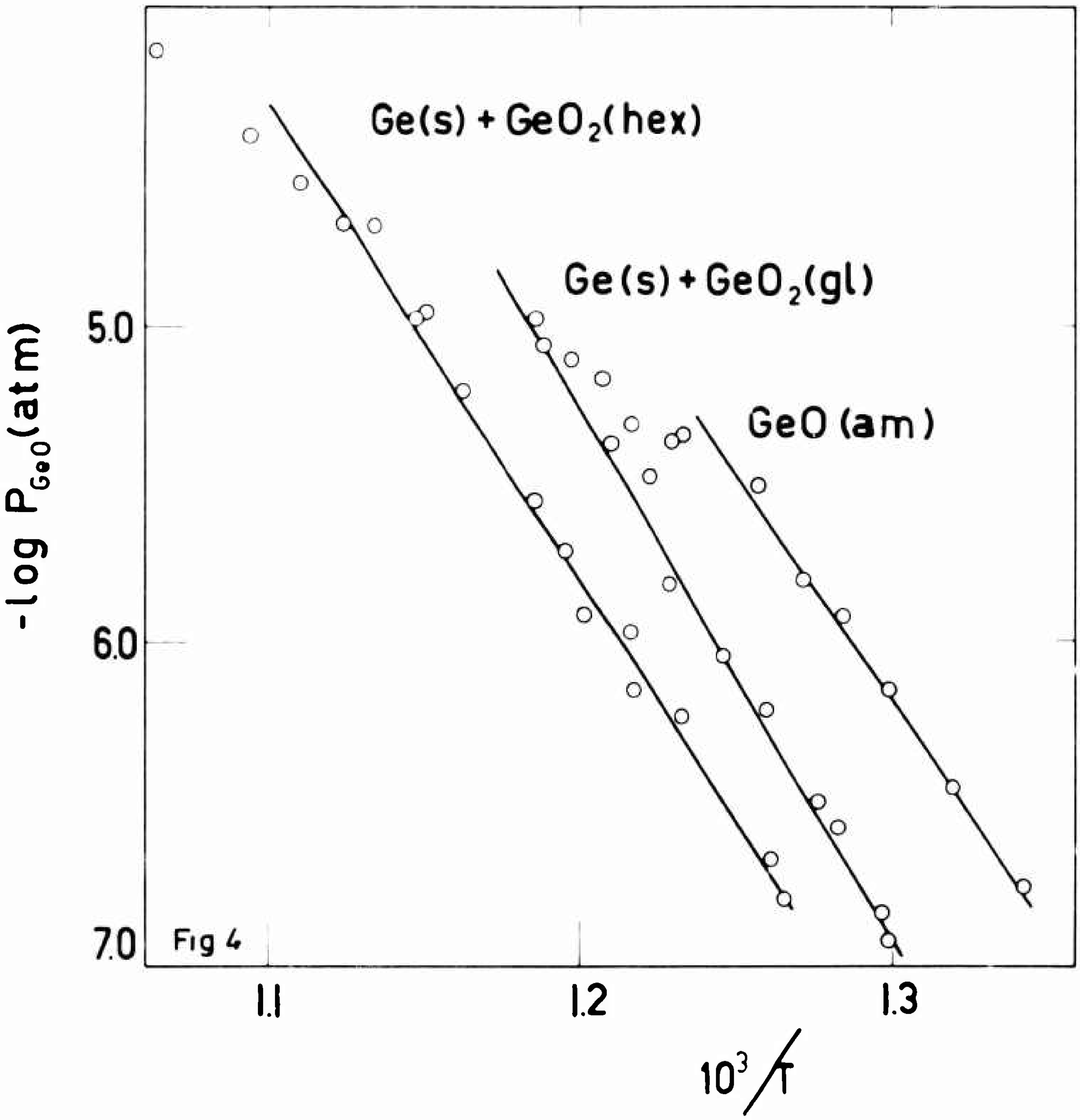

5
6
7
- log P (atm)
09.23
09.25
09.23
09.23
GeO
Ge_3O_3
Ge_2O_2
Fig.1
1.2
1.3
1.4
$10^3/T$


09.23
09.24
09.25
09.23
09.24
09.23
09.24
- log P (atm)
5
6
7
1.1
1.2
1.3
$10^3/T$
GeO
Ge_3O_3
Ge_2O_2
Fig.2

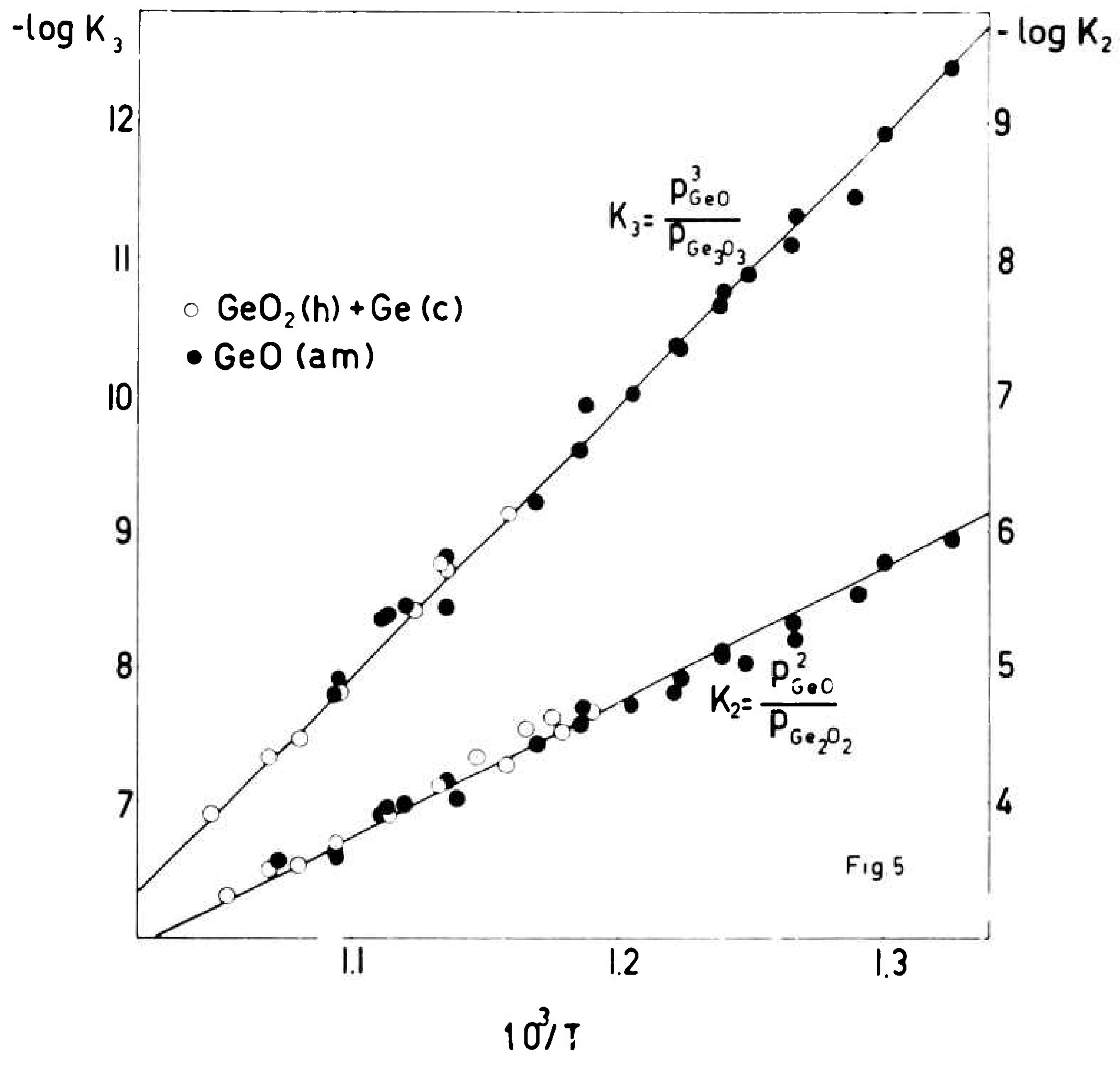


09.17
09.17
09.17
09.25
- log P (atm)
4
5
6
7
GeO
Ge_3O_3
Ge_2O_2
1.1
1.2
1.3
$10^3/T$

Fig.3



Ge(s) + GeO2(hex)
Ge(s) + GeO2(gl)
GeO (am)
-log P_GeO (atm)
5.0
6.0
7.0
Fig 4
1.1
1.2
1.3
10^3/T



-log K_3
- log K_2
12
11
10
9
8
7
9
8
7
6
5
4
$K_3 = \frac{p^3_{GeO}}{p_{Ge_3O_3}}$
$K_2 = \frac{p^2_{GeO}}{p_{Ge_2O_2}}$
○ GeO_2(h) + Ge (c)
● GeO (am)
Fig 5
1.1
1.2
1.3
$10^3/T$

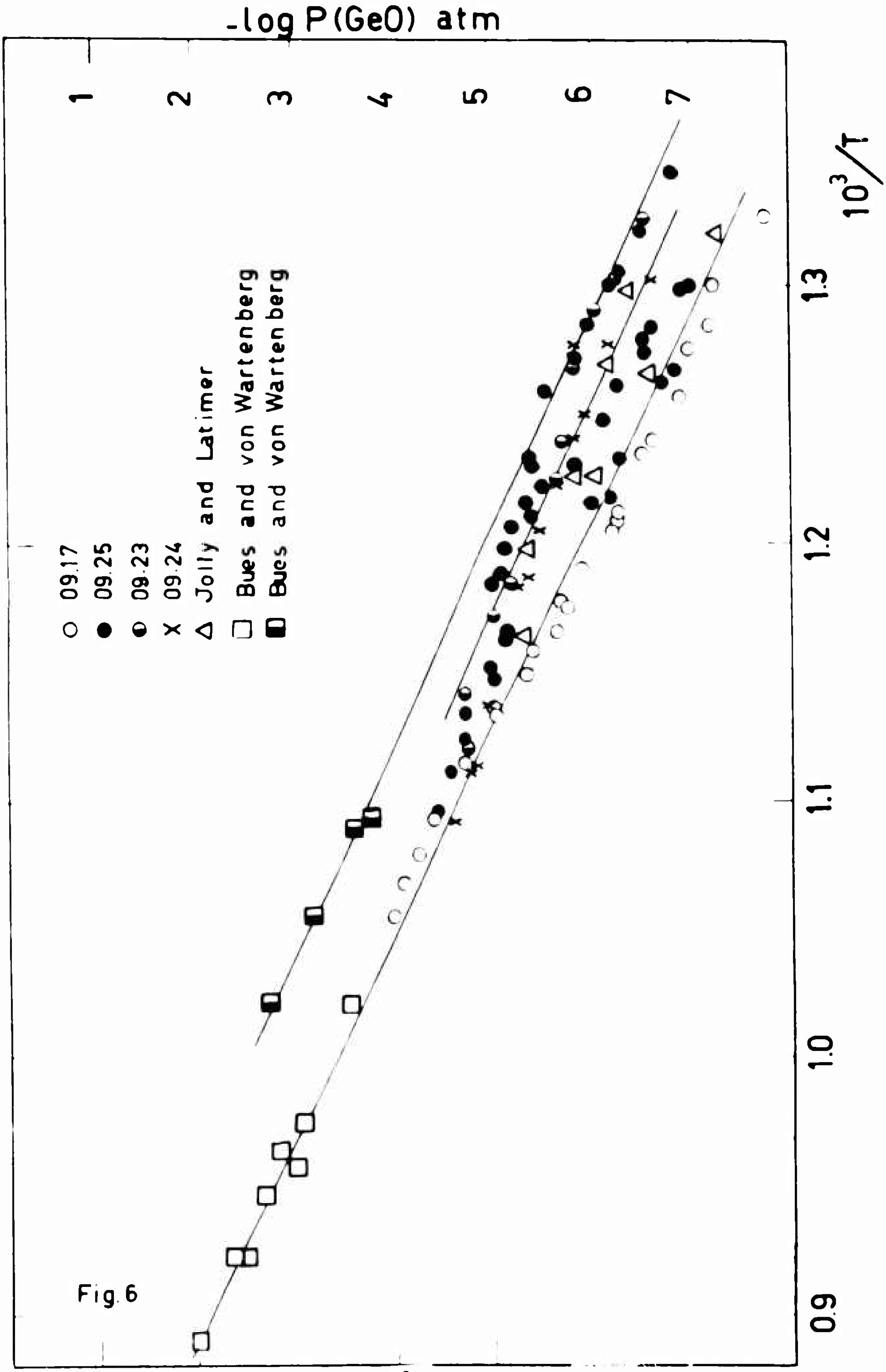

-log P(GeO) atm
1
2
3
4
5
6
7
09.17
09.25
09.23
09.24
Jolly and Latimer
Bues and von Wartenberg
Bues and von Wartenberg
0.9
1.0
1.1
1.2
1.3
10³/T

Fig. 6