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HEATS OF FORMATION OF GASEOUS METALLIC HALIDES.(U)
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June 1977



HEATS OF FORMATION OF GASEOUS METALLIC HALIDES

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Prepared by:

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I. INTRODUCTION

Reliable data for the gas phase reactions of the diatomic metal compounds are required to assess accurately the candidate species which are potentially significant to chemical laser technology for use by the Air Force in weaponry and defense systems. For example, the dissociation energies for a number of these diatomic oxides and halides are presently undetermined or uncertain. Thus the purpose of the studies conducted under this contract is to obtain experimental data with a high degree of accuracy for certain alkaline earth species important to chemical laser technology.

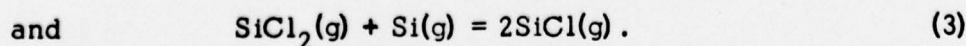
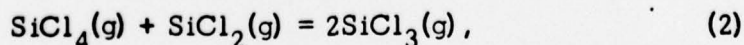
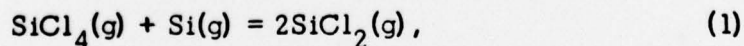
Thus far dissociation energies have been obtained for the diatomic alkaline earth oxides, BaO(g) , MgO(g) , SrO(g) and CaO(g) , for the alkaline earth monatomic halide MgCl(g) , and for SiF(g) and SiCl(g) . The heats of formation of $\text{SiF}_2\text{(g)}$, $\text{SiF}_3\text{(g)}$, $\text{SiCl}_2\text{(g)}$ and $\text{SiCl}_3\text{(g)}$ have also been obtained. Scientific papers involving these eleven species have already appeared or have been submitted for publication in the open literature. The results obtained under the past twelve months effort are described below and a comparison with previously published data is presented.

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II. RESULTS

A. Silicon Chlorides

The reaction of $\text{SiCl}_4\text{(g)}$ with Si(c) was studied in the temperature range 1593 to 1792°K. Second and third law reaction enthalpies were determined for



The third law heats of reaction, ΔH_{r298} , obtained were -30.4 ± 0.6 , 12.3 ± 0.5 and 27.1 ± 0.5 kcal/mole for reactions (1), (2) and (3), respectively.

The heats of reaction yielded third law ΔH_{f298} values of 47.1 ± 0.6 , -40.6 ± 0.6 and -93.3 ± 0.5 kcal/mole for SiCl(g) , $\text{SiCl}_2(\text{g})$ and $\text{SiCl}_3(\text{g})$, respectively. A third law dissociation energy value of 88.6 ± 0.6 kcal/mole was calculated for the dissociation of $\text{SiCl(g)} \longrightarrow (^3\text{P}_0)\text{Si(g)} + (^2\text{P}_{3/2})\text{Cl(g)}$. The second law ΔH_{f298} values from least squares plots of the intensity data (Fig. 1) were $\text{SiCl(g)} = 45.1 \pm 4$ kcal/mole, $\text{SiCl}_2(\text{g}) = -40.5 \pm 2$ kcal/mole and $\text{SiCl}_3(\text{g}) = -95.6 \pm 5$ kcal/mole.

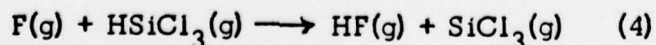
1. Heat of Formation of $\text{SiCl}_2(\text{g})$

The ΔH_{f298} value of -40.6 kcal/mole for $\text{SiCl}_2(\text{g})$ obtained in this study compares favorably with the results of transpiration experiments of Schafer, et al,^{1,2} (-38.2 kcal/mole), and of Teichmann and Wolf³ (-38.3 ± 2 kcal/mole). Other transpiration and static studies by Chechentsev, et al,⁴ Antipin and Sergeev,⁵ and Ishino, et al,⁶ yielded values for the ΔH_{f298} of $\text{SiCl}_2(\text{g})$ of -41 , -41.5 and -42.5 kcal/mole, respectively. The JANAF Tables⁷ recommend a value of -40 ± 1 kcal/mole from a review of these experimental results.

2. Heat of Formation of $\text{SiCl}_3(\text{g})$

Analyzing the electron impact studies of Steele, et al,⁸ who derived an average value for $\text{D}(\text{Cl}_3\text{Si-H})$ of 93 ± 4 kcal/mole, the JANAF Tables⁷ employed -122.6 kcal/mole for $\Delta H_{f298}(\text{Cl}_3\text{SiH(g)})$ and calculated $\Delta H_f \text{SiCl}_3 = -82$ kcal/mole, with an estimated uncertainty of approximately 10 kcal/mole. However, the JANAF Tables adopted -96 ± 10 kcal/mole for the ΔH_{f298} of $\text{SiCl}_3(\text{g})$ from comparisons with bond energies in the carbon halides and with linear plots of $\Delta H_f(\text{SiCl}_n)$ versus ΔH_f for SiF_n , CCl_n and CF_n .

Cadman, et al,⁹ from an examination of the infrared emission studies of Jonathan, et al,¹⁰ for the reaction



set limits to the ΔH of the reaction between -40.4 and -50.0 kcal and

chose -45.2 kcal, since they felt that the upper limit was the better estimate, and thus reported a value of -87.5 kcal/mole for the ΔH_{f298} of $\text{SiCl}_3(\text{g})$.

Additional non-equilibrium studies have been performed, including an electron impact study by Steele, et al,⁸ who calculated a value of -69 ± 4 kcal/mole for the ΔH_{f298} of $\text{SiCl}_3(\text{g})$ from ionization potentials and ion heat of formation. Wang, et al,¹¹ performed dissociative electron attachment experiments on $\text{SiCl}_4(\text{g})$ and assumed the formation of Cl^- and $\text{SiCl}_3(\text{g})$. Measuring an appearance potential for the Cl^- ion of 1.2 ± 0.2 eV and applying a correction of 7.6 kcal/mole for the excess vibrational and transitional energies they calculated a value of -81 ± 5 kcal/mole for ΔH_{f298} of $\text{SiCl}_3(\text{g})$. More recently, Pabst, et al, as reported by Franklin¹² from the same laboratory also employed dissociative electron processes and obtained -90 kcal/mole for the ΔH_{f298} of $\text{SiCl}_3(\text{g})$.

Generally, the electron collisional processes would be uncertain to at least ± 10 kcal/mole due to a lack of the positive identification of the ionic and radical species and the difficulty in precisely determining the excess energies involved in the process. Likewise, the kinetic processes involving silanes in reactions similar to equation (4) would have similar error limits. A discrepancy of at least 12 kcal/mole is seen from the values of -110 and -122.6 for the ΔH_{f298} for HSiCl_3 reported by Steele, et al,⁸ and the latest JANAF Table for this species (December 31, 1969), respectively.

3. Dissociation Energy of SiCl

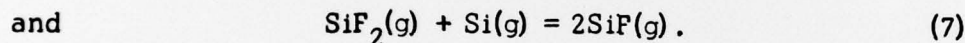
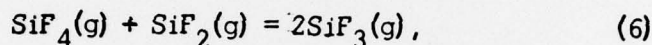
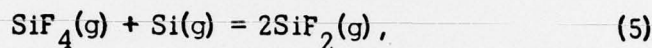
The dissociation energy for $\text{SiCl}(\text{g})$, 88.6 ± 0.6 kcal/mole (or 88.6 ± 2 kcal/mole, including error limits), obtained in these studies lies between those calculated from spectroscopic constants. The spectroscopic constants of Verma¹³ were examined by the JANAF Tables scientists,⁷ Gaydon,¹⁴ and Kuzyakov,¹⁵ with recommended values of 90 ± 15 , 76 ± 12 , and 103 ± 15 kcal/mole, respectively, for the dissociation energy of $\text{SiCl}(\text{g})$.

B. Silicon Fluorides

The reaction of $\text{SiF}_4(\text{g})$ with $\text{Si}(\text{c})$ was studied in the

temperature range 1590 - 1782°K. A double boiler Knudsen cell arrangement was used in which a stainless steel bulb containing SiF₄ was connected through an alumina tube with a 1 mm diameter annulus to an alumina effusion cell containing metallic silicon. The SiF₄ flow rate was controlled by a variable leak.

Second and third law reaction enthalpies were obtained for



The third law heats of reaction, ΔH_{f298} , determined were -2.9 ± 0.25 , 7.8 ± 0.5 and 21.1 ± 0.5 kcal/mole for reactions (5), (6) and (7), respectively. The heats of reaction yielded third law ΔH_{f298} values of -5.8 ± 0.5 , -140.6 ± 0.3 and -259.3 ± 0.5 kcal/mole for SiF(g), SiF₂(g) and SiF₃(g), respectively. A third law dissociation energy value of 131.2 ± 0.5 kcal/mole was calculated for the dissociation of $\text{SiF}(\text{g}) \rightarrow ({}^3\text{P}_0)\text{Si}(\text{g}) + ({}^2\text{P}_{3/2})\text{F}(\text{g})$. The second law ΔH_{f298} values obtained from intensity data (Fig. 2) were SiF(g) = -3.8 ± 5 kcal/mole, SiF₂(g) = -140.3 ± 2 kcal/mole, and SiF₃(g) = -259.5 ± 5 kcal/mole.

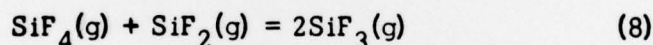
1. Heat of Formation of SiF₂(g)

The reaction of SiF₄ with Si(c) was studied in a flow system in the temperature range 1400 - 1600°K by Margrave, Kanaan and Pease.¹⁶ The product was assumed to be SiF₂ or its polymer. A heat of formation of -148 ± 4 kcal/mole for the ΔH_{f298} of SiF₂(g) was reported. Our studies showed that other silicon species account for approximately 30% of the total. From transpiration studies, Schafer, et al,¹ reported -139.0 kcal/mole for the ΔH_{f298} of SiF₂(g). Effusion-mass spectrometer experiments by Ehlert and Margrave¹⁷ involving the reaction of CaF₂ with silicon resulted in -140.5 ± 3 kcal/mole for the ΔH_{f298} of SiF₂(g),

in excellent agreement with the value of -140.6 ± 0.3 kcal/mole obtained in our studies.

2. Heat of Formation of $\text{SiF}_3(\text{g})$

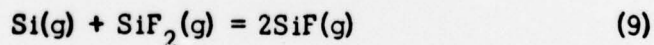
This is apparently the first thermochemical value for the ΔH_f of $\text{SiF}_3(\text{g})$. Two electron impact studies have yielded -235 ± 20 kcal/mole for the ΔH_{f298} .^{18,19} Wang, et al,¹⁹ reported this value from dissociative electron attachment processes to SiF_4 , while McDonald, et al,¹⁸ determined their value from electron impact studies on SiF_4 producing SiF_3^+ . In analyzing the work of McDonald, et al,¹⁷ and that of Wang, Margrave and Franklin¹⁹ the JANAF Supplement dated June 30, 1976 cites a paper by Franklin²⁰ in which he suggests that the assumption of the fraction of active vibrations as a constant in the previous electron impact studies may have caused a bias of 15 kcal/mole or more in the heat of formation. The JANAF Tables⁷ report an estimated value of -263 ± 5 kcal/mole assuming the ΔH of the reaction



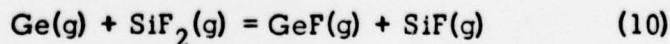
to be 0.5 kcal.

3. Dissociation Energy of SiF

Ehlert and Margrave¹⁷ in their effusion-mass spectrometer study also obtained ion intensity data for SiF^+ . With these data for the reaction



they reported 129.5 ± 3 kcal/mole for the D_o of SiF , which is in good agreement with the present value. Hastie and Margrave²¹ from the reaction enthalpy of



obtained 135 ± 3 kcal/mole for the D_o of SiF .

Johns and Barrow²² reported a value of 125 ± 10 kcal/mole

for the D_0 of SiF from a Birge-Sponer extrapolation of several spectroscopic states. Gaydon,¹⁴ on the other hand, obtained 115 ± 12 kcal/mole for the D_0 from a Birge-Sponer extrapolation of the ground state. Kuzyakov¹⁵ recommended 110 kcal/mole for the D_0 based on a review of the spectroscopic data.

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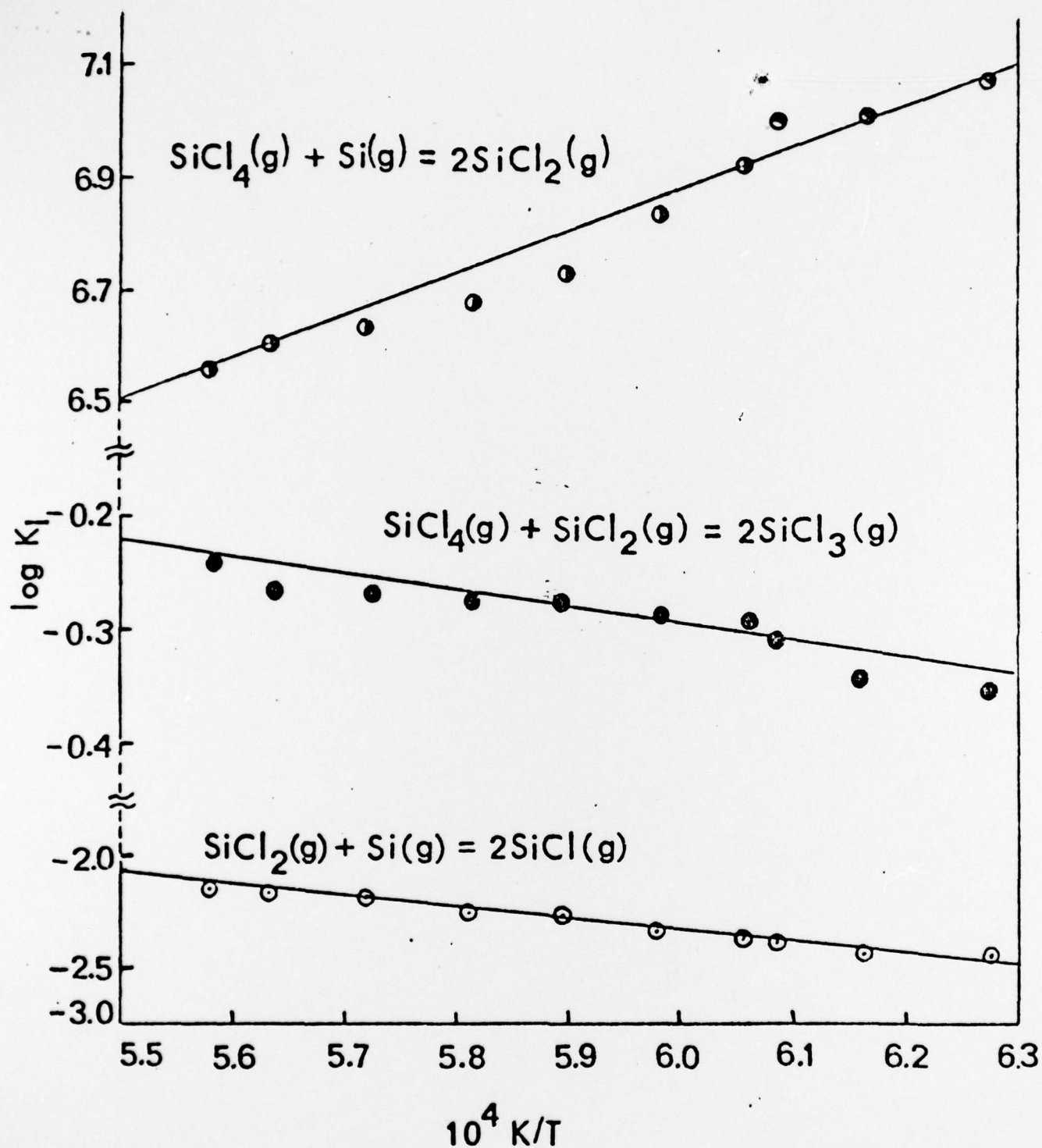


Fig. 1. Plots of the $\log K_I$ vs. $1/T$ for the Equilibria involved in the Reactions of $\text{Si}(\text{c})$ with $\text{SiCl}_4(\text{g})$

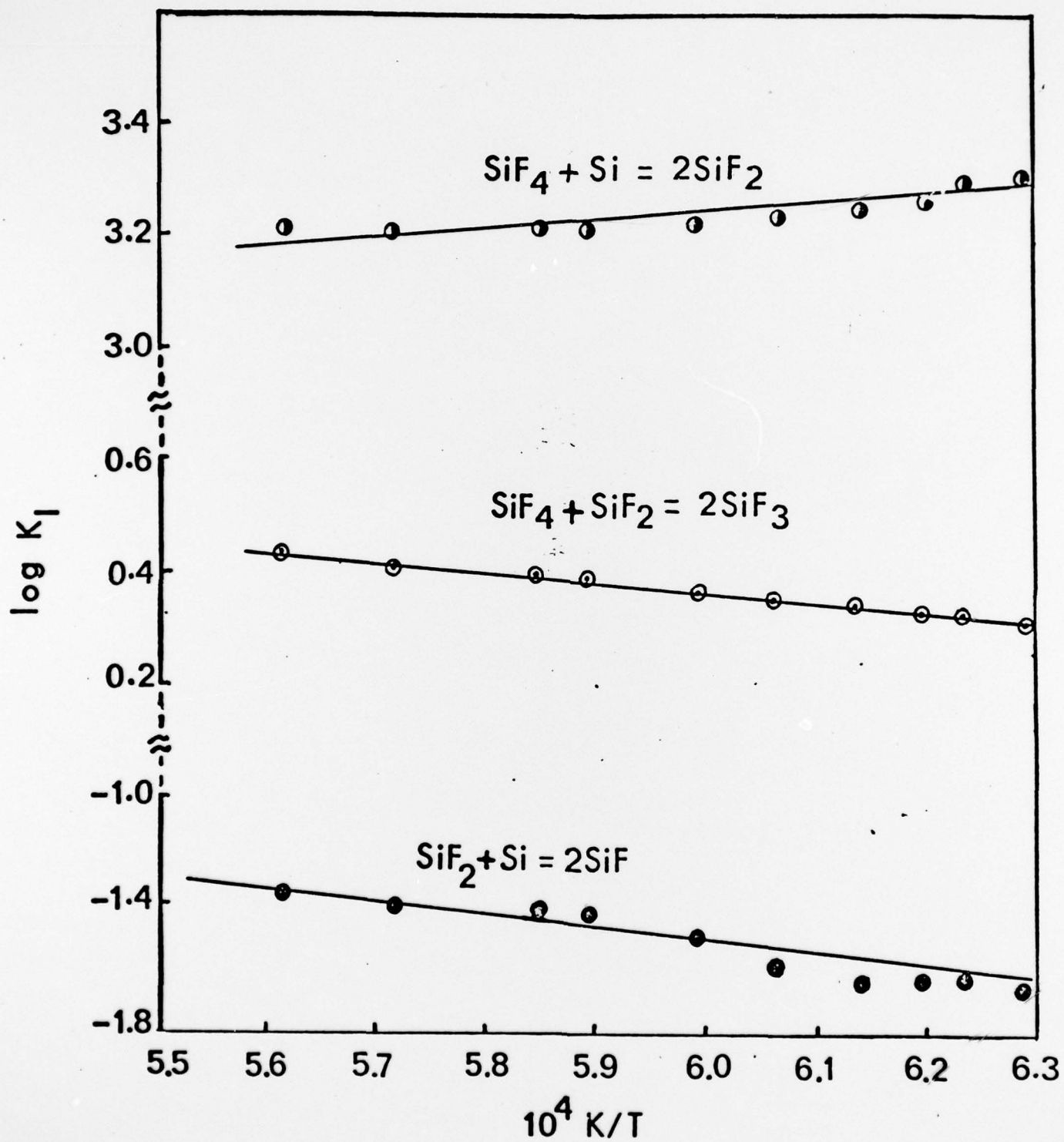


Fig. 2. Plots of the $\log K_I$ vs. $1/T$ for the gaseous isomolecular equilibria resulting from the reactions of Si(c) with $\text{SiF}_4(\text{g})$

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The heats of formation and dissociation energies for the silicon subchlorides and silicon subfluorides $\text{SiCl}_3(\text{g})$, $\text{SiCl}_2(\text{g})$, $\text{SiCl}(\text{g})$, $\text{SiF}_3(\text{g})$, $\text{SiF}_2(\text{g})$ and SiF were determined from high temperature thermochemical reactions of $\text{SiCl}_4(\text{g})$ and $\text{SiF}_4(\text{g})$. Ion intensities for the species involved in the reactions were obtained mass spectrometrically, leading to equilibrium constants and reaction enthalpies. The heats of formation were obtained by both second and third law methods and found to be in good agreement.			

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