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Rare-earth sulfides at high temperature. I. On the existence of equilibrium in Knudsen cells*

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Two different approaches have been used to investigate whether gaseous equilibrium exists above solid mixtures and to study whether measurements of equilibrium constants can be accomplished inside a Knudsen cell. Both were mass spectrometric studies of isomolecular exchange reactions of rare-earth sulfides. The first was a study of a single reaction generated in different chemical systems containing different condensed reacting phases and thus yielding different sulfur chemical potentials. The second was a study of a reaction in the presence and absence of a third condensed substance. The results demonstrated that gaseous equilibrium was achieved in the cell for these particular systems. The opinion is expressed that similar studies should be performed on chemical systems being used for studies of isomolecular exchange reactions. In order that measurements on such reactions can be reliably made, the solids should have comparable volatility, and the gases should have comparable dissociation energies.

INTRODUCTION

No extensive study has been published concerning the existence of gas phase equilibrium above a solid sample in mass spectrometric isomolecular exchange reactions, although this technique has been widely used in recent years to yield dissociation energies of high-temperature molecules.

In 1968 Cater, Rauh, and Thorn[1] reported mass spectrometric investigations of solid mixtures of US and UO_2 in which the measurements were less precise and reproducible than in previous studies of simpler systems with the same equipment. They attributed this fact to non-equilibrium conditions in the condensed phases. Their experience suggests that it is deceptive to assume that calculated "equilibrium constants" correspond to an observation of a gaseous equilibrium in such a system. They pointed out that since the mean free paths of gaseous molecules generally are larger than the dimensions of the cell, the effusates come not from gas phase collisions but rather from the surface of the sample. Also they suggested that in a system of two or more solid phases in which the condensed phases undergo slow, long-term changes in composition, in which different areas of the sample surface may be at different compositions and in which the location of small regions of phase may change, nonreproducible results may occur.

In 1971, Hampson and Gilles[2] demonstrated that gaseous equilibrium was established in their isomolecular oxygen exchange reactions with a solid mixture of Ge, Sc_2O_3, and $TiO_{1.15}$. They found that values for the equilibrium constants for the Sc—Ti—O exchange reaction were the same in both the sample-containing and empty compartments of a twin cell. These values were also the same when a solid mixture of Ti and Sc_2O_3 was used.

The purpose of the present paper is to investigate whether gaseous equilibrum does exist inside a Knudsen cell for isomolecular exchange reactions under conditons such that no collisions occur in the gaseous phase. Two approaches were used. The first method was to study the equilibrium constant at different temperatures for a particular isomolecular gaseous reaction involving two metals and sulfur in systems with different solid phases giving significantly different sulfur chemical potentials. The second approach was to study equilibrium constants at different temperatures of an isomolecular gaseous reaction involving two metals and sulfur both before and after the vaporization to exhaustion of a different, more volatile sulfide.

EXPERIMENTAL

Samples and Analysis

The seven samples, YS, SmS, SmS_x, EuS, GdS, $\gamma-Gd_2S_3$, and HoS were prepared from the elements. The rare-earth metal ingots used were purchased from the rare-earth division of American Potash and Chemical Corporation, Chicago, Illinois, and had a quoted purity of 99.9%. The crystalline sulfur used was obtained from the Gallard-Schlesinger Chemical Manufacturing Corporation, Carleplace, New York, and had a purity of 99.999%.

The metal powder was obtained by filing down the ingots inside a dry box filled with an atmosphere of argon and using a magnet to remove any iron resulting from the filing process. The solid rare-earth sulfide samples were synthesized by heating of appropriate ratios of rare earth and sulfur in a sealed, evacuated Vycor tube (less than 20 μ) at about 800 °C inside a resistance furnace for several days. Each residue was then ground and annealed in an inductively heated tungsten crucible under background pressures of 10^{-5}—10^{-6} torr at above 1600 °C for several hours. Each sample was analyzed by the x-ray Debye—Scherrer powder diffraction method. Chemical analysis was performed on the samples of GdS and Gd_2S_3. All the rare-earth monosulfides possess a cubic structure of the NaCl type.

A detailed description of the samples follows: (1) The YS sample was a yellow substance with a lattice parameter of 5.4931 ± 0.0003 Å, a value in agreement with 5.493 Å given by Guittard.[3] (2) The EuS – 2 sample was annealed three times; it was a shiny-gray substance with a lattice parameter of 5.9679 ± 0.0006 Å, a value nearly in agreement with 5.966 Å given by Iandelli and Palenzona.[4] (3) The SmS_x sample was reddish in appearance. The x-ray diffraction pattern gave weak diffraction lines corresponding to Sm_3S_4 and other phases. (4) The SmS sample was the residue of the SmS_x sample which was annealed under high vacuum at 1600 °C for 1 h. It was a black substance with a lattice parameter of 5.9677 ± 0.0007 Å, a value in agreement with 5.967 Å given by Houston.[5] (5) The GdS – 3(h) sample, the residue from run MS – 7, was annealed several times; it was a gold-metalic substance with a lattice parameter of 5.5618 ± 0.0006 Å, a value in agreement with 5.562 Å given by Guittard.[3] The chemical composition was determined to be $GdS_{1.06\pm0.04}$.[5] The $\gamma-Gd_2S_3-2$ sample was a gray substance with a lattice parameter of 8.3723 ± 0.0005 Å (Th_3P_4-type structure), a value to be compared with 8.387 Å given by Flahaut *et al.*[6] The chemical compositon was $GdS_{1.56\pm0.03}$.[7] The HoS sample was a red-violet substance with a lattice parameter of 5.4467 ± 0.0004 Å, a value to be compared with 5.457 Å given by Guittard.[3] This sample showed some weak diffraction lines corresponding to a phase having a Th_3P_4-type structure.

Mass Spectrometer

The mass spectrometer used in this study was a Nuclide first-order direction focusing instrument with a 12 in. radius, 60° magnetic sector. A pulse-counting technique was used for measuring the ion intensity of each species. The apparatus has been previous described.[2,7] Three cylindrical tungsten crucibles were used. The orifice dimensions and the preparation method are presented in Table I. Column 1 gives the laboratory designated number. Column 2 describes the fabrication method. Column 3 gives the average area of the orifice. Columns 4 and 5 list the length and the length-to-radius ratio of the orifice. The last column gives the Clausing factors calculated from the equation of Freeman and Edwards.[8]

Procedure

An appropriate mixture of two or three substances of interest was placed in a tungsten crucible inside the mass spectrometer and heated by electron bombardment. The temperature was measured directly by sighting the optical pyrometer (No. 3) into the blackbody hole of the crucible. After the mixture had been heated at about 1500 °C overnight, the ionization efficiency curve of each species was recorded on an X—Y recorder. From the curves an appropriate electron energy was chosen to minimize fragmentation. In order to resolve overlapping peaks, an appropriate isotope was chosen for each species.

At each temperature the ion intensity of each species was measured for five 5-sec intervals with the shutter open, similarly with shutter closed, and again with shutter open. The numbers of these counts were then printed and punched on paper tape. After completion of the experiment, the data were stored on magnetic tape No. HTCHEM 90348. The equilibrium constant for the isomolecular reaction was then calculated to be the product of the ratios of the ion intensities (number of counts/5 sec), by assuming that the product of ionization cross sections was unity. The residue left inside the crucible after the experiment was analyzed using the x-ray diffraction method.

The detailed experimental conditions are given in Table II. Column 1 gives the experimental run number. Column 2 lists the amounts of condensed samples used. Column 3 and 4 give the crucible number and electron energy which was the same for all species, respectively. The last column lists the experimental temperature range.

RESULTS

Method Ia: Effect of Solid Phases on Gaseous Equilibria
(a) Sm–Gd–S

Table III summarizes the results for the reaction,

$$GdS(g) + Sm(g) = SmS(g) + Gd(g). \qquad (1)$$

TABLE I. Orifice dimensions of the tungsten crucibles.

Crucible No.	Prep. method	Area (10^{-3} cm^2)	Length (cm)	l/r	Clausing factor
104	drill	4.01	0.126	3.53	0.387
107	elox	6.72	0.128	2.77	0.445
110	drill	5.19	0.121	2.95	0.423

TABLE II. Experimental conditions for mass spectrometric isomolecular sulfur exchange reactions of rare earths.

Expt.	Samples	Crucible used	Electron energy (eV)	Temp range (°K)
MS-11	GdS-3 h(51.56 mg.), HoS(57.80 mg.) and SmS_x (49.80 mg.)	W-110	12	2057—2278
MS-14	γ-Gd_2S_3(451.62 mg.), SmS(201.35 mg.)	W-107	12	2077—2296
MS-15	Gd(173.10 mg.), SmS(200.90 mg.)	W-107	12	2119—2177
MS-16	GdS-3 h(50.80 mg.), SmS(110.51 mg.)	W-107	12	2148—2319
MS-13(a)	GdS-3 h(40.37 mg.), EuS-2(42.07 mg.)	W-104	11	2002—2219
MS-13(b)	Gd(516.70 mg.), EuS-2(323.73 mg.)	W-104	11	1598—2150
MS-9	GdS-3 h(43.66 mg.), YS(31.33 mg.)	W-110	71, 12	1991—2294

The first column lists the experimental run number. Column 2 gives the samples used. Column 3 lists the experimental temperature range. Column 4 and 5 give the slope and intercept with their standard deviations of the least squares line. The last column gives the number of data used for the least squares analysis.

A plot of log*K* vs $1/T$ for this reaction is given in Fig. 1. The plot shows that within a factor less than 2, the equilibrium constant at a given temperature, when it can be reliably measured, is independent of the specific solid phases present; the table shows that the slopes and intercepts of the log*K* vs $1/T$ plots from the different systems are the same. The results for the individual experiments are described below.

MS-11, GdS + HoS + SmS_x

At the beginning of this experiment, the relative intensities of the species at 2181 °K were: $Sm^+:Gd^+:Ho^+:SmO^+:GdO^+:HoO^+:SmS^+:GdS^+:HoS^+ = 320:3:92:5:1:12:24:19:8$. The samarium species disappeared and the SmS_x was presumably exhausted halfway through this experiment, thus only limited data pertaining to Reaction (1) were available. A total of 11 data points was obtained. The three highest-temperature points were excluded in the least squares treatment because too little samarium sulfide was present to produce saturation under conditions of high flow rate. A mass of 87.34 mg was vaporized out of a total sample of 159.16 mg. The residue was a molten gray substance. The x-ray diffraction pattern of the residue showed two phases present: A phase having a Th_3P_4-type structure with a lattice parameter of 8.38 ± 0.03 Å; a phase giving a diffraction pattern similar to that of isostructural β-Nd_2S_3 reported by Picon *et al.*[9]

MS-14, γ-Gd_2S_3 + SmS

In the early stages of this experiment the relative intensities of the species at 2077 °K were: $Gd^+:Sm^+:GdO^+:SmO^+:GdS^+:SmS^+ = 2:4125:1:18:11:47$. No noticeable change in the chemical composition of the solid sample was observed during ion intensity measurements at a given temperature as shown by the time-independent intensities of the four ion species Sm^+, Gd^+, SmS^+, and GdS^+, monitored during the experiment. The gaseous reaction (1) was studied over a temperature range of 220 °K, resulting in small uncertainties in the second-law enthalpy and entropy. A mass of 105.97 mg of the mixture was vaporized out of a total of 652.97 mg. The residue appeared to be molten and gray in color. The x-ray diffraction pattern showed the residue to have a Th_3P_4-type structure with a lattice parameter of 8.364 ± ± 0.007 Å. This experiment is believed to give the most reliable results for obtaining the thermodynamic data.

MS-15, Gd + SmS

There was no detectable SmS^+ in the mass spectrum at the beginning of this experiment. The relative intensities of the observed ion species at 2013 °K were: $Sm^+:Gd^+:GdO^+:GdS^+ = 400:100:1:1$. The intensities of Gd^+ and Sm^+ were found to decrease with time. The ion SmS^+ was observed in the mass spectrum with very weak intensity at 2119 °K. At the end of this experiment, both Sm^+

TABLE III. Effect of solid phases on the reaction, $GdS(g) + Sm(g) = SmS(g) + Gd(g)$; $\log K = -10^3 A/T + B$.

Expt.	Samples	Temp range (°K)	Slope (*A*)	Intercept (*B*)	No. of data
MS-11	$GdS + SmS_x + HoS$	2134—2231	11.1 ± 1.9	2.68 ± 0.85	8
MS-14	γ-Gd_2S_3 + SmS	2077—2296	10.8 ± 1.1	2.57 ± 0.51	30
MS-15	Gd + SmS	2119—2177	···	···	2
MS-16	GdS + SmS	2195—2294	10.1 ± 2.6	2.32 ± 1.17	16

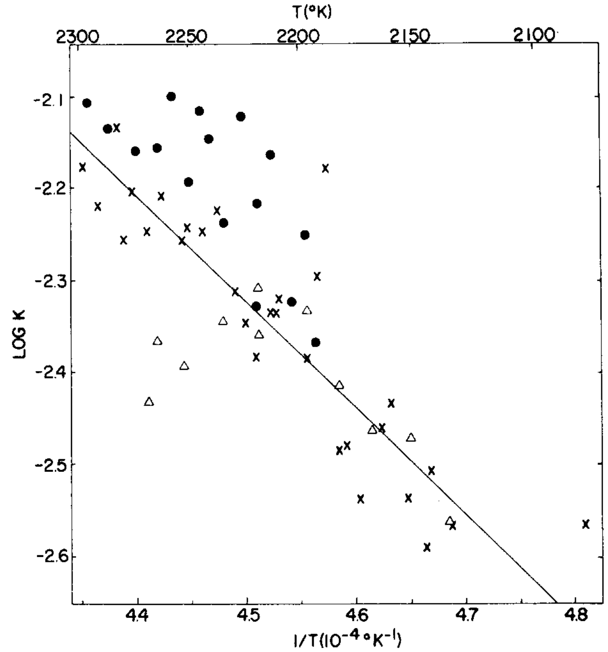

FIG. 1. Values of equilibrium constants for the reaction $\mathrm{GdS(g)+Sm(g)=SmS(g)+Gd(g)}$. Triangles represent data from MS-11 in which the samples were GdS, SmS_x, and HoS; ×'s, MS-14, γ-$\mathrm{Gd_2S_3}$, and SmS; circles, MS-16, GdS, and SmS. The line is the linear least squares result for MS-14, the experiment believed to be most reliable. Points represented by three triangles in left center were not included in least squares analysis for reasons described in text.

and SmS$^+$ were not observed, while the ion signals of Gd$^+$, GdS$^+$, and GdO$^+$ remained at constant values with the ratio of 8:2:1, respectively, at 2177 °K. Hence, no reliable equilibrium constant for the Gd—Sm—S reaction can be obtained in this experiment. A total of 172.39 mg of the original 374.0 mg mixture was vaporized. The residue appeared to have been unmelted and was golden in color. The x-ray diffraction pattern showed the residue to have a NaCl-type structure with a lattice parameter of 5.5644 ± 0.0003 Å indicative of GdS with perhaps a small amount of SmS.

MS-16, GdS+SmS

The relative intensities of the species at 2136 °K were: Gd$^+$:Sm$^+$:GdO$^+$:SmO$^+$:GdS$^+$:SmS$^+$ = 1:4100:1:30:6:159. Due to the difference in the volatilities of the two solid phases GdS and SmS, there was a large decrease of the more volatile phase (SmS) during the time required to measure the intensities of the four species, resulting in a large uncertainty in the calculation of the equilibrium constants. A total of 21 data points was obtained; only 16 data points were used in the least squares calculations because of large uncertainties introduced into one lowest-temperature point in the beginning of the experiment and the four highest-temperature points near the end of the experiment. A total of 108.71 mg was vaporized out of the original 161.31 mg. The residue appeared to have been melted; the surface of the residue was gray; and the bottom of the residue was golden in color. The x-ray diffraction pattern showed the residue to have a $\mathrm{Th_3P_4}$-type structure with a lattice parameter of 8.3768 ± 0.0001 Å.

Method Ib: Effect of Solid Phases on Gaseous Equilibria
(b) Eu-Gd-S

Attempts were made to study the reaction,

$$\mathrm{GdS(g)+Eu(g)=EuS(g)+Gd(g)}, \tag{2}$$

but reliable equilibrium constants were not obtained from the solid mixtures of GdS + EuS and of Gd + EuS because the intensities of one or more species were too low. These results reveal one of the constraints on the choice of the chemical system. The results for the individual experiments are presented below.

MS-13(a), GdS+EuS

At the beginning of this experiment, only the Eu$^+$ ion was observed in the mass spectrum at 1876 °K. The EuS$^+$ began to appear when the temperature was 2002 °K. The intensities of GdS$^+$ and Gd$^+$ were too low to be measured accurately. At the end of the experiment, the relative intensities of the species at 2219 °K were: Eu$^+$:Gd$^+$:EuO$^+$:GdO$^+$:EuS$^+$:GdS$^+$ = 1800:14:1:2:13:42. The intensity of Eu$^+$ was found to decrease with time, and finally vanish in the mass spectrum at

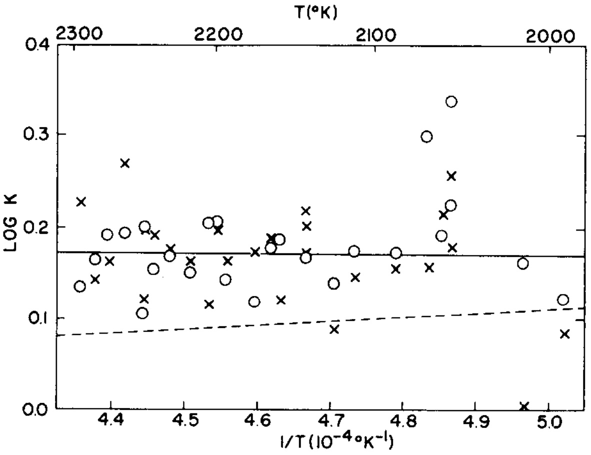

FIG. 2. Values of equilibrium constants for the reaction, $\mathrm{GdS(g)+Y(g)=YS(g)+Gd(g)}$. Crosses represent data from MS-9 with solid phases GdS and YS at 12 eV; circles, 71 eV. The solid line is the linear least squares result of all the data; the dashed line is that of Smoes *et al.*[10] taken at 20–25 eV from solid phases Gd and YS.

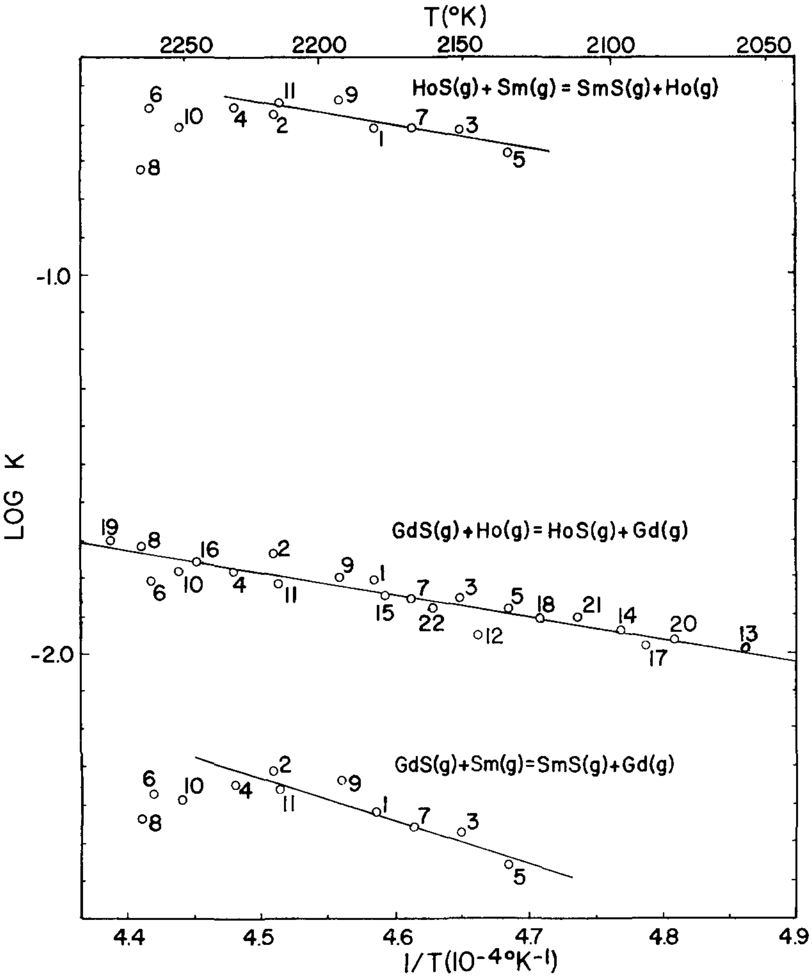

FIG. 3. Values of equilibrium constants for gaseous isomolecular exchange reactions in MS-11. Solid materials were GdS, HoS, and SmS_x through point 11; only the first two later. Lines are linear least squares results with the three highest-temperature points omitted for samarium reactions because too little samarium sulfide was present to maintain saturation at the high flow rates.

2248 °K. There were only three equilibrium constants available, and they were not very reliable. A total of 39.98 mg of the total sample weight of 82.44 mg was vaporized. The residue appeared to have been melted and gray in color. The residue was identified as a phase having a Th_3P_4-type structure with a lattice parameter of 8.386 ± 0.004 Å.

MS-13(b), Gd+EuS

At the beginning of the experiment, only the Eu^+ ion was observed in the mass spectrum at 1598 °K. The intensity of Eu^+ was found to decrease with time, and finally drop to zero at 1710 °K. At the end of the experiment, the relative intensities of Gd^+, GdO^+, and GdS^+ were found to be 150, 2, and 1, respectively, at 2150 °K. Hence, no equilibrium constants for this reaction were available in this experiment. The residue appeared to have been melted and formed an alloy-type substance which adhered strongly to the crucible; a few golden spots and some gray material were observed on the surface. An x-ray diffraction pattern was taken of the surface material. Only front diffrac-

TABLE IV. Effect on the partial pressures of Gd(g), GdS(g), Ho(g), and HoS(g) and on calculated equilibrium constants for the reaction, GdS(g) + Ho(g) = HoS(g) + Gd(g), with and without the presence of SmS_x.

Expt	Temp	Ion intensity (counts/5 sec)				K
no.	(°K)	Gd(158)	Ho(165)	GdS(190)	HoS(197)	(10^{-2})
1[a]	2181	102 ± 11	11 803 ± 111	605 ± 25	1034 ± 33	1.56 ± 0.19
3[a]	2151	94 ± 10	11 513 ± 108	503 ± 23	819 ± 29	1.41 ± 0.18
15[b]	2177	262 ± 17	31 488 ± 181	983 ± 32	1584 ± 42	1.42 ± 0.11
22[b]	2161	327 ± 21	33 331 ± 186	1046 ± 33	1317 ± 43	1.31 ± 0.09

[a] Prior to the disappearance of samarium species from mass spectrum.
[b] After the disappearance of samarium species from mass spectrum.

tion lines were obtained, indicating an NaCl-type structure with a lattice parameter of 5.553 ± 0.002 Å, which was a metal-rich $Gd_{1+x}S$ phase.

Method Ic: Effect of Solid Phases on Gaseous Equilibria (c) Y–Gd–S

Present results may be compared with those of Smoes, Coppens, Bergman, and Drowart[10] on the gaseous reaction,

$$GdS(g) + Y(g) = YS(g) + Gd(g), \quad (3)$$

in which different solid phases were used. Smoes *et al.* studied the vaporization of a mixture of YS and Gd metal from a molybdenum Knudsen cell. In the present study, MS – 9, an equimolar mixture of GdS and YS in a tungsten cell was used. At the beginning of the experiment, the relative intensities of the observed ion species at 2044 °K were: $Y^+:Gd^+:YO^+:GdO^+:YS^+:GdS^+ = 138:218:1:21:62:78$.

As illustrated in Fig. 2, the values for the equilibrium constant for the exchange reaction (3) from the two studies agree with each other to within about 20%, and hence, values for the equilibrium constant are independent of the solid phases present.

Method II: Effect of Other Materials (SmS_x) on Gaseous Equilibrium Gd–Ho–S

The three samples used in MS – 11 for studying the gaseous reaction,

$$GdS(g) + Ho(g) = HoS(g) + Gd(g), \quad (4)$$

were GdS, HoS, and SmS_x. After point 11, the solid sample of SmS_x was presumed exhausted. While SmS_x was present, the gaseous reaction (4) was studied at a temperature range 2134–2267 °K. After the disappearance of SmS_x, the partial pressures of the above four species increased, hence this reaction was studied over a wider temperature range 2057–2278 °K.

Table IV presents the equlibrium constants of Reaction (4) both with and without the presence of SmS_x at nearly the same temperature. Column 1 lists the experimental run number. Column 2 gives the temperature at which the data were taken. Columns 3–6 give the ion intensities of the gaseous species, $Gd^+(158)$, $Ho^+(165)$, $GdS^+(190)$, and $HoS^+(197)$, respectively, in counts per 5 sec. The errors represent the standard deviations. The last column giving the value of the equilibrium constant for Reaction (4) shows that it has the same value within about 10% at a given temperature regardless of whether the third phase is present.

A plot of $\log K$ vs $1/T$ for this reaction is given in Fig. 3. The results from the same experiment are shown also for the samarium reactions for which the three highest temperature points lie lower than the line probably because too litte samarium sulfide was present to produce saturation under conditions of high flow rate.

The results of this experiment show that although the partial pressures of each species GdS(g), Gd(g), Ho(g), and HoS(g) were affected by the presence of the solid sample SmS_x, values of the equilibrium constant for Reaction (4) remain the same both with and without the third solid present.

DISCUSSION

This paper is a study of the question of whether equilibrium exists in Knudsen cells and of the related question of whether measurements of an equilibrium system may be accomplished.

In the present work seven different combinations of seven rare-earth sulfides and gadolinium metal were studied mass spectrometrically at low electron energy. Relative to the monosulfide composition, some of the solid mixtures were metal rich, some stoichiometric, and some sulfur rich; in some, displacement reactions occurred in the solid. Equilibrium constants were measured for several gaseous isomolecular exchange reactions.

Within a factor of 2, the equilibrium constant for a reaction was independent of the specific solid phases present even though significant differences in sulfur chemical potential occurred. We conclude that for these systems, equilibrium did exist in the knudsen cell for these isomolecular exchange reactions. Similar studies should probably be performed with any chemical system being used for studies of isomolecular reactions. Independence of measured equilibrium constants on sample character and initial composition is a familiar and convincing demonstration of the existence of chemical equilibrium.

The second question is to examine the conditions that must exist in order that reliable constants for isomolecular exchange reactions may be measured. The system must be at equilibrium, and the pressures of the species must be large enough to be measured. These pressures are determined by the properties of both the solid phases and gaseous molecules. Reliable exchange equilibrium constants may result from mass spectrometric measurements if the system has the following properties: The solid phases should possess approximately equal volatility, because a large difference in volatility can cause a rapid decrease in pressures of some species during the actual time required to make a measurement. The two gaseous molecules should possess similar dissociation energies, because a great difference will cause the partial pressure of one of the gaseous molecules to be too low to be measured accurately.

The results presented herein are being combined with absolute measurements on gadolinium sulfide to give thermodynamic information.

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