Partial Pressures of Strontium and Strontium Oxide over Strontium Oxide Heated on Platinum

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A quadrupole mass filter was used to determine the partial pressures of Sr(g) and SrO(g) over strontium oxide heated on a platinum-ribbon filament. The ion currents of $^{88}Sr^+$ and $^{88}Sr^{16}O^+$ were measured while the filament temperature was continuously increasing at a heating rate of about 14°C/min; the calculations of the partial pressures were carried out by the integral method for Sr(g) and by the sensitivity-calibration method for SrO(g). The data are represented by:

$$\log P_{\mathrm{Sr(g)}}(\mathrm{atm}) = 6.633 - \frac{2.536\times10^4}{T}$$

in the temperature range of 1643—1851°K, and by:

$$\log P_{\mathrm{SrO(g)}}(\mathrm{atm}) = 6.707 - \frac{2.793\times10^4}{T}$$

in the 1747—1850°K range. From the values of the partial pressures, the dissociation energy of strontium oxide was determined to be $D_0°(\mathrm{SrO})=96.2\pm0.9$ kcal/mol by the third-law treatment and $D_0°(\mathrm{SrO})=102\pm5$ kcal/mol by the second-law treatment.

Many studies have been carried out on the nature of vapor species from strontium oxide heated on various materials, such as platinum,[1–3] tungsten,[4–5] molybdenum,[4] and alumina.[7] Using mass-spectrometric techniques, Aldrich,[1] Bickel and Holroyd,[2] and Pelchowitch[3] have observed that, in the strontium oxide-platinum system, the main vaporization products are free strontium atom, plus small amounts of the strontium oxide molecules, and that no reactions occur between strontium oxide and platinum. However, the partial pressures of Sr(g) and SrO(g) could not be determined, since no sensitivity calibration of their mass spectrometers was done. Drowart *et al.*[4,5] have measured the relative ion intensities of the vapor products produced by the reactions of alkaline earth oxides with a tungsten Knudsen cell or molybdenum cell, and determined the dissociation energy of alkaline earth oxides and the stabilities of the gaseous tungstates, tungstites, molybdates, and molybdites of alkaline earths. Recently, the present authors[6] measured the partial pressures of Sr(g), SrO(g), $SrWO_4$(g), and $SrWO_3$(g) over the solid products produced by the reactions between strontium oxide and a tungsten-ribbon filament. Porter *et al.*[7] also measured the partial pressure of SrO(g) in equilibrium with the solid placed in an alumina Knudsen cell only at the temperature of 2100°K.

Hitherto, the vapor pressure over strontium oxide heated on a platinum filament have all[8,9] been determined on the assumption that SrO(g) is the only gaseous species, although experimental evidence to justify this assumption has never been published.

In the present work, a quadrupole mass filter was used to determine the partial pressures of Sr(g) and SrO(g) over strontium oxide heated on a platinum-ribbon filament. The ion currents of $^{88}Sr^+$ and $^{88}Sr^{16}O^+$ were measured while the filament temperature was continuously increasing at a constant rate; the partial pressures were calculated by the integral method for Sr(g) and by the sensitivity-calibration method for SrO(g). Moreover, from the values of the partial pressures, the dissociation energy of strontium oxide was determined by third-law and second-law treatments.

In a conventional integral method,[10] the ion currents are ordinarily measured at a fixed temperature or by varying the temperature step by step for a proper interval, while in the present work the currents were measured under the above conditions, since the measurements were carried out with a very small sample.

The vaporization of strontium oxide supported on various materials is of interest in the physics and chemistry concerned with the phenomena of the thermal emissions of electrons and ions.

Experimental

The platinum-ribbon filament used to hold the strontium oxide was 0.75 mm wide and 0.025 mm thick (H. Cross. Co.) and was kept straight with the aid of a tungsten spring, even at high temperatures.

Strontium nitrate was used to prepare strontium oxide on the filament. Reagent-grade strontium nitrate was

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[1] L. T. Aldrich, *J. Appl. Phys.*, **22**, 1168 (1951).

[2] P. W. Bickel and L. V. Holroyd, *J. Chem. Phys.*, **22**, 1793 (1954).

[3] I. Pelchowitch, *Chem. Abstr.*, **48**, 7963f (1954); *Phillips Research Repts.*, **9**, 42 (1954).

[4] J. Drowart, G. Exsteen, and G. Verhaegen, *Trans. Faraday Soc.*, **60**, 1920 (1964).

[5] G. Verhaegen, R. Colin, G. Exsteen, and J. Drowart, *ibid.*, **61**, 1372 (1965).

[6] Y. Yamamoto, M. Asano, N. Sasaki, and K. Kubo, *Meeting of the Mass Spectroscopy Society of Japan*, Tokyo, May, 1970.

[7] R. F. Porter, W. A. Chupka, and M. G. Inghram, *J. Chem. Phys.*, **23**, 1374 (1955).

[8] G. E. Moore, H. W. Allison, and J. D. Struthers, *J. Chem Phys.*, **18**, 1572 (1950).

[9] A. Claassen and C. F. Veenemans, *Z. Phys.*, **80**, 342 (1933).

[10] R. T. Grimley, "The Characterization of High-Temperature Vapors," ed. by J. L. Margrave, John Wiley and Sons, New York (1967), p. 193.

purified by the carbonate method and was crystallized out from a nitrate solution. Using a micro syringe, 1 μl of strontium nitrate solution containing 20.30 μg of strontium was placed on the central part of the filament for a length of about 3 mm and dried under an infrared lamp. After it had then been set in a vacuum chamber, the filament was slowly heated by an externally-programmed DC power supply driven by a motor of an adjustable speed; the strontium nitrate was thus thermally decomposed to strontium oxide. Then, the filament was further heated at a rate of about 14°C/min, and the partial pressures of the gaseous species vaporized from the strontium oxide on the platinum filament were measured by means of a NEVA NAG 510H quadrupole mass filter equipped with a secondary electron multiplier.

A collimated gaseous beam originating from strontium oxide was ionized in an ionization chamber by low-energy electrons (13 eV), so the fragmentation of SrO(g) to Sr^+ and O was assumed to be negligible.

The filament holder was devised so as to move back and forth; this mechanism was used as a shutter.

A schematic diagram of the arrangement of the experimental apparatus is shown in Fig. 1.

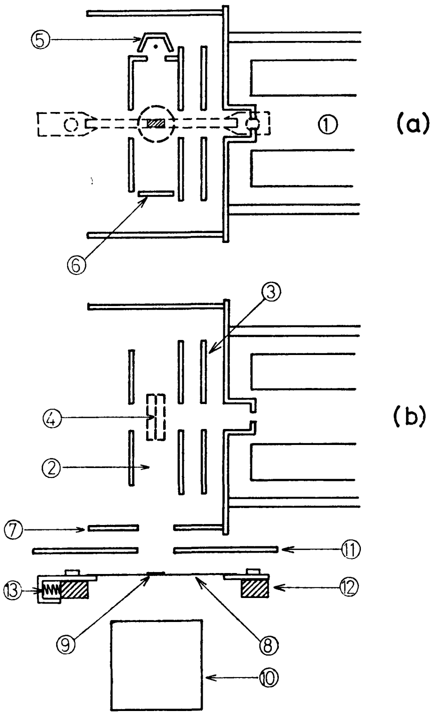

Fig. 1. Schematic diagram of the arrangement of experimental apparatus.
(a) Upper view and (b) side view.
1) quadrupole mass analyser 2) ionization chamber 3) ion focusing plate 4) filament for electron emission 5) electron repeller 6) electron trap 7) beam collimator 8) platinum ribbon filament 9) sample 10) prism 11) shield 12) filament holder 13) spring

The filament temperature was measured with a Leed and Northrup 8632C optical pyrometer by sighting the back side of the filament, on which strontium oxide was applied, through a prism; the readings were corrected for the emissivity of the platinum filament and the transmission coefficients of the prism and the glass window of the vacuum chamber. If an appreciable thermal gradient existed throughout the sample, the results might be seriously in error. Under the present conditions, however, the error seems to be negligible because of the very small sample.

The background pressure in a vacuum chamber was maintained at less than 2×10^{-8} Torr with an ion pump during all the experiments.

The basic data of the present work are the ion-current measurements of $^{88}Sr^+$ and $^{88}Sr^{16}O^+$ made with a continuosly-increasing temperature at a heating rate of about 14°C/min. The upper temperature limit was dictated by the amount of the sample, and the lower limit, by the ion-detection ability of the mass filter.

The resolution of a quadrupole mass filter varies automatically throughout mass scanning, so that the sensitivity varies with the mass number. The mass filter used in this study was designed to maintain a constant relation between sensitivity and resolution. Consequently, for a given resolution, the ion current is quantitatively proportional to the number of ionizable gaseous atoms. To obtain this relation, the ion currents of the $M/e=28$, 44, 71, 85, and 109 peaks were measured as a function of the resolution. The resolution is here defined as $M/\Delta M$, where M is the mass number and where ΔM is the half-width of the ion peak in amu. The relations for the five ion species are shown in Fig. 2, where the slopes are constant. In the present work, the resolution was kept high enough to measure the ion currents of Sr^+ and SrO^+, usually higher than 130.

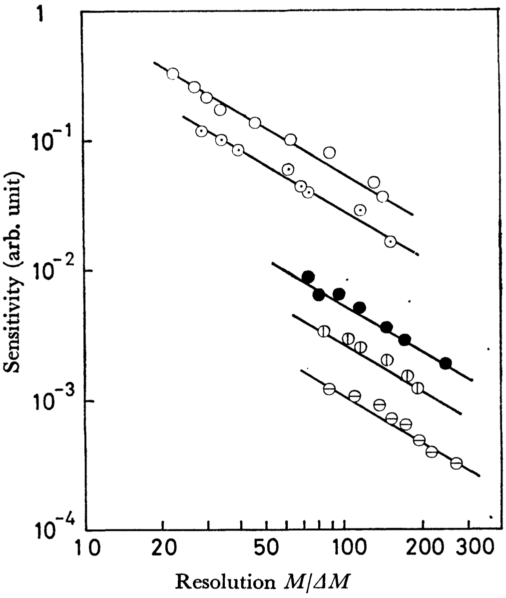

Fig. 2. Relation between sensitivity and resolution. $M/e=$ 28 (⊙), 44 ○, 71 ●, 85 ⦶, and 109 ⊖.

The background ions of the same mass number as the interesting species resulted from the residual gases in a vacuum chamber. However, the effect of the background was practically negligible at higher temperatures, since the ion intensities of Sr^+ and SrO^+ were much greater than the residual gas ions.

Method for Determining Partial Pressures

The determination of the vapor pressures of solid materials with a mass spectrometer has been carried out by two methods, namely, the sensitivity-calibration method[10-12] and the integral method.[10,11] In the

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[11] W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

[12] J. Drowart, G. DeMaria, R. P. Burns, and M. G. Inghram, *J. Chem. Phys.*, **32**, 1366 (1960).

latter method, a known amount of sample is completely vaporized out and the ion intensity is integrated over the period of time required to vaporize the entire sample. Knowing the whole amount of sample vaporized and making use of the vaporization equation, the vapor pressure of the sample is calculated. The modified integral method was used to calculate the partial pressure of Sr(g).

The total number of gaseous atoms (or molecules), z_{tot}, vaporized from the sample is given by:

$$z_{\text{tot}} = a\int_0^{t_{\text{end}}} z\,\mathrm{d}t \tag{1}$$

where z is the number of gaseous atoms vaporized per unit of time per unit of area, where a is the vaporization area, and where t_{end} is the time after which the sample is completely vaporized out. The ion current, I^+, is given by the following relation:

$$I^+ = C\frac{(E-I)\sigma\gamma S_1 S_2}{\bar{v}}z \tag{2}$$

where C is the factor for instrument geometry, E is the energy of the impact electron, I is the ionization potential of the element (or compound), σ is the maximum ionization cross section of the gaseous species, γ is the isotopic abundance ratio for the ionized gaseous species, S_1 is the efficiency of the electron multiplier, S_2 is the sensitivity of the mass filter, and $\bar{v}$ is the average velocity of the gaseous atoms.

From Eqs. (1) and (2), the following equation is obtained:

$$z_{\text{tot}} = \frac{a}{C(E-I)\sigma\gamma S_1 S_2}\int_0^{t_{\text{end}}} I^+\bar{v}\,\mathrm{d}t \tag{3}$$

Since, in the present work, the ion currents are measured with a continuously increasing temperature at a constant rate, the $\bar{v}$ is given as a function of the time:

$$\bar{v} = \sqrt{\frac{8\boldsymbol{R}T_t}{\pi M}} \tag{4}$$

where $\boldsymbol{R}$ is the gas constant and where T_t is the sample temperature at time t. Substituting for $\bar{v}$, Eq. (3) becomes:

$$z_{\text{tot}} = K\int_0^{t_{\text{end}}} I^+\sqrt{T_t}\,\mathrm{d}t \tag{5}$$

where:

$$K = \frac{a}{C(E-I)\sigma\gamma S_1 S_2}\sqrt{\frac{8\boldsymbol{R}}{\pi M}}$$

Similarly, the number of gaseous atoms, $z_{\Delta t}$, vaporized in the time interval between t_1 and t_2, during which the temperature increases from T_1 to T_2, is given by:

$$z_{\Delta t} = K\int_{t_1}^{t_2} I^+\sqrt{T_t}\,\mathrm{d}t \tag{6}$$

Taking the ratio of Eqs. (5) and (6):

$$\frac{z_{\Delta t}}{z_{\text{tot}}} = \frac{W_{\Delta t}}{W_{\text{tot}}} = \frac{\int_{t_1}^{t_2} I^+\sqrt{T_t}\,\mathrm{d}t}{\int_0^{t_{\text{end}}} I^+\sqrt{T_t}\,\mathrm{d}t} \tag{7}$$

where W_{tot} is the whole amount of the sample and where $W_{\Delta t}$ is the amount vaporized in the time interval $\Delta t = t_2 - t_1$. The graphical integrals in Eq. (7) are shown in Fig. 3, where the experimental data for only the Sr^+ ion current are given against the time, together with the temperature. The whole area under the curve of $I^+\sqrt{T_t}$ corresponds to W_{tot}, and the oblique line part area, to $W_{\Delta t}$. Consequently, the rate of the vaporization of atoms vaporized per unit of time per unit of area, m, is obtained from the following equation:

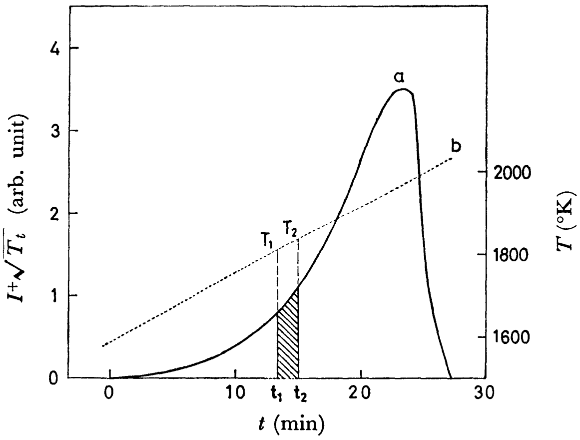

Fig. 3. Graphical representation for the integrals in Eq. (7).
(a) $I_{\text{Sr}^+}\sqrt{T}$ and (b) temperature.
Whole area under the curve (a) is corresponded to the integral of the denominator and oblique line part area to the numerator in Eq. (7).

$$m = \frac{W_{t}}{a\Delta t} = \frac{W_{\text{tot}}}{a\Delta t}\,\frac{\text{oblique-line part of Fig. 3}}{\text{whole area of Fig. 3}} \tag{8}$$

For the vaporization from an open surface, the vapor pressure, P, at the average temperature of $\bar{T} = (T_1 + T_2)/2$ in the time interval of Δt can be calculated by the Langmuir equation[13]:

$$P = m\sqrt{\frac{2\pi\boldsymbol{R}\bar{T}}{M}} \tag{9}$$

assuming the vaporization coefficient to be unity. Then, for a series of time intervals, the vapor pressures are successively calculated in the same manner, until the amount of sample decreases and the rate of vaporization does not give the pressure corresponding to the temperature.

When a vaporization occurs in only one vapor species the above procedure can be applied to the measurement of the vapor pressure without any correction. In the case of the vaporization of strontium oxide on the platinum filament, however, the strontium-containing vapors consists of a predominant amount of Sr(g) and a small amounts of SrO(g), as is shown in Fig. 4, where the experimental data for the Sr^+ and SrO^+ ion currents from their vapors are given. Consequently, in the present work the SrO^+ ion current was first converted into an imaginary strontium ion current, $I^+_{\text{Sr}}(\text{imag})$, which was equivalent to I^+_{SrO}; then, by using the sum of the actual and the imaginary strontium ion currents, $I^+_{\text{Sr}}(\text{sum}) = I^+_{\text{Sr}} + I^+_{\text{Sr}}(\text{imag})$, the integral of the denominator in Eq. (7) was carried out. In this case, Eqs. (8) and (9) become:

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[13] L. Langmuir, *Phys. Rev.*, **2**, 329 (1913).

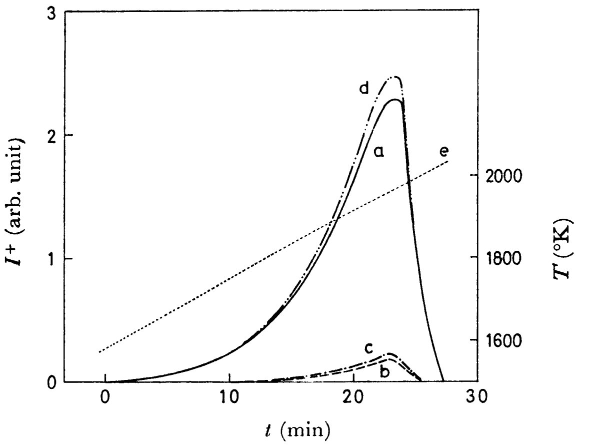

Fig. 4. Experimental data for $I^+{}_{\mathrm{Sr}}$ and $I^+{}_{\mathrm{SrO}}$ against time, together with $I^+{}_{\mathrm{Sr}}$ (imag) and $I^+{}_{\mathrm{Sr}}$(sum).
(a) —— $I^+{}_{\mathrm{Sr}}$, (b) ----- $I^+{}_{\mathrm{SrO}}$, (c) — — — $I^+{}_{\mathrm{Sr}}$ (imag) equivalent to $I^+{}_{\mathrm{SrO}}$, (d) — - - — $I^+{}_{\mathrm{Sr}}$ (sum) $= I^+{}_{\mathrm{Sr}} + I^+{}_{\mathrm{Sr}}$ (imag), and (e) ------ temperature.

$$m_{\mathrm{Sr}} = \frac{W_{\mathrm{Sr}}\ \text{in SrO}}{a\Delta t}\,\frac{\int_{t_1}^{t_2} I_{\mathrm{Sr}}^+\sqrt{T_t}\,\mathrm{d}t}{\int_0^{t_{\mathrm{end}}} I_{\mathrm{Sr}}^+(\mathrm{sum})\sqrt{T_t}\,\mathrm{d}t} \tag{10}$$

and:

$$P_{\mathrm{Sr}} = m_{\mathrm{Sr}}\sqrt{\frac{2\pi \boldsymbol{R}\bar{T}}{M_{\mathrm{Sr}}}} \tag{11}$$

respectively. The values of $I^+{}_{\mathrm{Sr}}$ (imag) and $I^+{}_{\mathrm{Sr}}$ (sum) are also shown in Fig. 4.

The conversion of $I^+{}_{\mathrm{SrO}}$ into $I^+{}_{\mathrm{Sr}}$ (imag) was carried out as follows. When SrO(g) is vaporized from strontium oxide, the current of the strontium oxide ion is given from Eq. (2):

$$\begin{aligned} I_{\mathrm{SrO}}^+ &= C\frac{(E-I_{\mathrm{SrO}})\sigma_{\mathrm{SrO}}\gamma_{\mathrm{SrO}}S_{1\mathrm{SrO}}S_{2\mathrm{SrO}}}{\bar{v}_{\mathrm{SrO}}}z_{\mathrm{SrO}} \\ &= k\frac{(E-I_{\mathrm{SrO}})\sigma_{\mathrm{SrO}}\gamma_{\mathrm{SrO}}S_{1\mathrm{SrO}}S_{2\mathrm{SrO}}\sqrt{M_{\mathrm{SrO}}}}{\sqrt{T}}z_{\mathrm{SrO}} \end{aligned} \tag{12}$$

where $k=C\sqrt{\pi/8\boldsymbol{R}}$.
Similarly, for the imaginary strontium ion:

$$I_{\mathrm{Sr}}^+(\mathrm{imag}) = k\frac{(E-I_{\mathrm{Sr}})\sigma_{\mathrm{Sr}}\gamma_{\mathrm{Sr}}S_{1\mathrm{Sr}}S_{2\mathrm{Sr}}\sqrt{M_{\mathrm{Sr}}}}{\sqrt{T}}z_{\mathrm{Sr}}(\mathrm{imag}) \tag{13}$$

Now, if the $^{88}\mathrm{Sr}^+$ and $^{88}\mathrm{Sr}^{16}\mathrm{O}^+$ are measured, the following relations hold:

$$z_{\mathrm{SrO}} = z_{\mathrm{Sr}}(\mathrm{imag}) \tag{14}$$

and:

$$\gamma_{\mathrm{SrO}} = \gamma_{\mathrm{Sr}} \tag{15}$$

Consequently, from Eqs. (12) and (13):

$$I_{\mathrm{Sr}}^+(\mathrm{imag}) = \frac{(E-I_{\mathrm{Sr}})\sigma_{\mathrm{Sr}}S_{1\mathrm{Sr}}S_{2\mathrm{Sr}}\sqrt{M_{\mathrm{Sr}}}}{(E-I_{\mathrm{SrO}})\sigma_{\mathrm{SrO}}S_{1\mathrm{SrO}}S_{2\mathrm{SrO}}\sqrt{M_{\mathrm{SrO}}}}I_{\mathrm{SrO}}^+ \tag{16}$$

That is, the amount of $I^+{}_{\mathrm{SrO}}$ at a given temperature can be converted into the $I^+{}_{\mathrm{Sr}}$(imag) using Eq. (16).

For the calculation of the partial pressure of SrO(g), the sensitivity-calibration method was employed. Here, the partial pressure of Sr(g) was used as a reference; that is:

$$P_{\mathrm{SrO}} = \frac{I_{\mathrm{SrO}}^+(E-I_{\mathrm{Sr}})\sigma_{\mathrm{Sr}}S_{1\mathrm{Sr}}S_{2\mathrm{Sr}}T_{\mathrm{SrO}}}{I_{\mathrm{Sr}}^+(E-I_{\mathrm{SrO}})\sigma_{\mathrm{SrO}}S_{1\mathrm{SrO}}S_{2\mathrm{SrO}}T_{\mathrm{Sr}}}P_{\mathrm{Sr}} \tag{17}$$

In the mass-spectrometric Knudsen effusion technique, silver has been widely used as a reference material, since silver vaporizes almost entirely in the form of monoatomic gases and the vapor pressure is well known. However, in the present condition of free vaporization from an open surface, it is difficult to use an outer reference such as silver.

The values of the ionization potentials for strontium and strontium oxide were taken from Drowart[4] to be $I_{\mathrm{Sr}}=5.7$ and $I_{\mathrm{SrO}}=6.1$ eV, while the relative maximum ionization cross section for strontium was taken from Mann[14] to be $\sigma_{\mathrm{Sr}}=8.88$ and the cross section for strontium oxide was obtained, by summing the values for the constituent atoms, as $\sigma_{\mathrm{SrO}}=10.19$. The efficiency of the electron multiplier for the mass dependence, S_1, was corrected by a factor of the reciprocal of the square root of the mass number, taking into account the so-called mass effect.[15] Moreover, the sensitivity of the mass filter, varying with the resolution, S_2, was corrected from the constant slope of the lines in Fig. 2. As the time interval, Δt, 1 min was taken for all calculations.

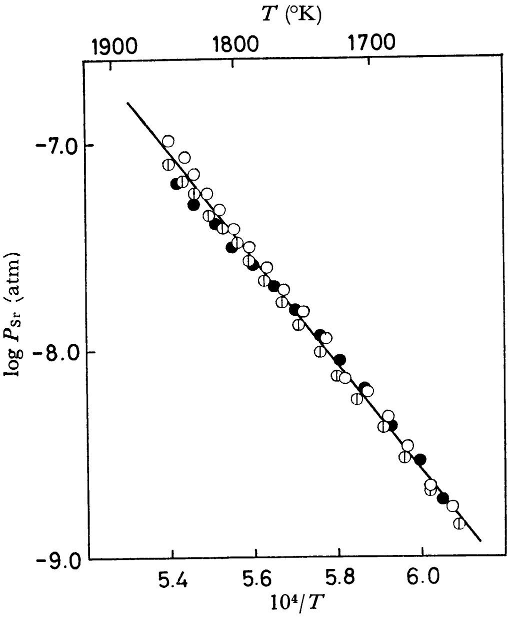

Fig. 5. Partial pressure of Sr(g) over strontium oxide heated on platinum. Run 1 ○, run 2 ●, and run 3 ◐.

Results and Discussion

1. *Partial Pressure of Sr(g).* The partial pressures of Sr(g) over strontium oxide heated on a platinum filament are shown in Fig. 5. The line drawn by the least-squares treatment of the data follows this equation:

$$\log P_{\mathrm{Sr}}(\mathrm{atm}) = 6.633 - \frac{2.536\times 10^4}{T} \tag{18}$$

in the temperature range of 1643—1851°K. Moreover, from the slope of the line the heat of the vaporization of Sr(g)[16] was calculated to be 116±2 kcal/mol at the

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[14] J. B. Mann, *J. Chem. Phys.*, **40**, 1646 (1967).

[15] W. Ploch and W. Walcher, *Rev. Sci. Instrum.*, **22**, 1028 (1951).

[16] This value corresponds to the partial molar enthalpy of the vaporization of Sr(g) from SrO(g).

experimental temperatures. Here, the uncertainty is the standard deviation for the least-squares fit.

As will be described later, the partial pressure of Sr(g) is more than an order of magnitude greater than that of SrO(g). Consequently, it may be observed that the total vapor pressures over strontium oxide obtained by Moore *et al.*,[8] and by Claassen and Veenemans,[9] assuming SrO(g) to be the only gaseous species, are approximately equivalent to the partial pressure of Sr(g) if the consideration of a factor of $\sqrt{M_{\mathrm{Sr}}/M_{\mathrm{SrO}}}$ is made for their values. The agreement between the observed partial pressure of Sr(g) and their total vapor pressures is extremely good.

In the experiments of Moore *et al.* and of Claassen and Veenemans, the vaporization took place in sealed-off tubes, so the Sr(g) vaporized from the heated sample to the cold collector wall could readily recombine with the released oxygen. Thus, even though strontium oxide was found in the collected products on the wall, the calculations should be carried out for each vapor species of Sr(g) and SrO(g) by the aid of mass analysis.

Bickel and Holroyd[2] have described that the temperature dependence of the Sr^+ ion current is at first seemingly irreproducible. However, the sample passes through a series of changes as the temperature is cycled, and eventually equilibrium conditions are reached on the platinum filament, where reproducible data can be obtained. They have also determined the heat of the vaporization of Sr(g) from the slopes of the lines obtained by plotting the log Sr^+ ion current against the reciprocal of the temperature; they found it to be 164 kcal/mol in the initial state, and 60 kcal/mol for the higher-temperature range and 138 kcal/mol for the lower in the final state. However, Aldrich[1] has observed that the vaporization process of strontium oxide heated on platinum is reproducible without any particular care, and from similar plots of his data he obtained the heat of the vaporization of Sr(g) as 144 kcal/mol over the full temperature range investigated. In the present work, where the measurements were carried out with a continuously increasing temperature, the Sr^+ and SrO^+ ion currents were satisfactorily reproducible in all runs.

Further, the heat of the vaporization of SrO(g) has been obtained by Moore *et al.*, from their data on the total vapor pressure, to be 126.6 kcal/mol, while Blewett,[17] from the data of Claassen and Veenemans,[9] found it to be 117 kcal/mol. Again, these values are approximately equivalent to the value for Sr(g). The agreement of the heats of the vaporization of Sr(g) determined by many workers is poor.

2. Partial Pressure of SrO(g). The partial pressures of SrO(g) vaporized congruently from strontium oxide on platinum are shown in Fig. 6. The line represents the least-squares fit of the data of three runs and is given by the following equation:

$$\log P_{\mathrm{SrO}}(\mathrm{atm}) = 6.707 - \frac{2.793\times10^4}{T} \tag{19}$$

in the temperature range of 1747—1850°K. Moreover, the heat of the vaporization of SrO(g) was calculated to be 128±2 kcal/mol at the experimental temperatures.

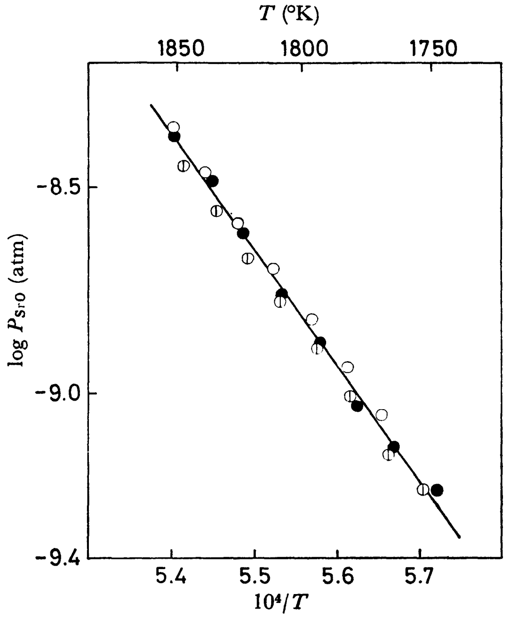

Fig. 6. Partial pressure of SrO(g) over strontium oxide heated on platinum. Run 1 ○, run 2 ●, and run 3 ◐.

Here again, the uncertainty given is the standard deviation for the least-squares fit.

The measurements for the vapor pressure and for the heat of vaporization of SrO(g) have been carried out by Porter *et al.*[7] only at the temperature of 2100°K, using a mass-spectrometric Knudsen effusion method with an alumina cell. The vapor pressure of 2.5×10^{-7} atm for SrO(g), obtained by extrapolating the line in Fig. 6 to 2100°K, may be seen to be in conflict with the value of 3.8×10^{-8} atm estimated by Porter *et al.* at this temperature; also, the heat of vaporization, 135±3 kcal/mol, corrected to 298°K, is in poor agreement with their value of 155.1 kcal/mol at 298°K. These discrepancies seem to be due to the difference in the supporting materials for strontium oxide and/or the uncertainty as to their experimental error for the single measurement at 2100°K.

The reactions between strontium oxide and platinum have been studied thermodynamically by Moore *et al.*[8]

Their results indicate that strontium oxide and platinum do not react in such a manner as to form free Sr(g), and at the same time they do not produce any compounds containing strontium and platinum. In the present work, no high-mass compounds resulting from a reaction between strontium oxide and platinum were detected, although some Pt^+ ions were observed at the highest temperature.

3. Dissociation Energy of Strontium Oxide. For the experimental determination of the dissociation energy of strontium oxide, it is necessary to measure the partial pressures of Sr(g), SrO(g), and oxygen in the present system. The mass spectra of O^+ and $\mathrm{O_2}^+$ ions exhibited a more indistinct shutter effect than those of the Sr^+ and SrO^+ ions did, so the partial pressure of oxygen was calculated from the following relation:

$$P_{\mathrm{O}}(\mathrm{atm}) = \sqrt{\frac{M_{\mathrm{O}}}{M_{\mathrm{Sr}}}}P_{\mathrm{Sr}}(\mathrm{atm}) = 0.4273P_{\mathrm{Sr}}(\mathrm{atm}) \tag{20}$$

assuming that the oxygen atoms were vaporized by an

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[17] J. P. Blewett, *J. Appl. Phys.*, **10**, 668 (1939).

equivalent amount of Sr(g) at a given temperature. If oxygen molecules are assumed to be in equilibrium with Sr(g) and SrO(g), half of the dissociation energy of the oxygen molecule must be considered in the calculations.

The free-energy function for SrO(g) was calculated from the usual statistical mechanical equations[18] by using the data of the vibration frequency of strontium oxide, $\omega=653.5$ cm^{-1} [19]; the interatomic distance, $r=1.921$ Å[19], and the electronic states, $^3\Sigma$ and $^3\Pi$, lying about 10870 cm^{-1} above the ground state, $X^1\Sigma$.[4] The values calculated are $-(G_T^\circ-H_0^\circ)/T=60.4$(1500°K), 60.9 (1600°K), 61.4(1700°K), 61.9(1800°K), 62.4(1900°K), and 62.8(2000°K) in cal/mol deg respectively. The free-energy functions for Sr(g) and O(g) were taken from Margrave.[20]

By combining the free-energy functions of SrO(g), Sr(g), and O(g) with the free-energy change for the following reaction:

$$\mathrm{SrO(g) = Sr(g) + O(g)} \qquad (21)$$

the dissociation energy was calculated to be $D_0^\circ(\mathrm{SrO})=96.2\pm0.9$ kcal/mol. Moreover, a least-squares fit to the second-law treatment for the equilibrium constant of the same reaction gave $D_{1800}^\circ(\mathrm{SrO})=103\pm5$ kcal/mol, which became $D_0^\circ(\mathrm{SrO})=102\pm5$ kcal/mol when corrected to 0°K by using the heat capacities of SrO(g), Sr(g), and O(g). Here, the heat capacity of SrO(g) was calculated by the use of the kinetic theory.[21]

In general, the analysis of the data by third-law treatment is considered superior to that using the second law because each data point is independent of the other.

The dissociation energy of strontium oxide has been determined by various methods, that is, mass-spectrometric measurements by the Langmuir method and the Knudsen effusion method, total vapor-pressure measurements, spectrometric measurements, and theoretical calculations. In Table 1, the values determined in this work are shown together with the literature values. The values obtained by the present mass-spectrometric Langmuir method agree, within the limits of experimental error, with those obtained by the Knudsen method except for the low value reported by Porter *et al.*,[7] As for this low value, Drowart *et al.*[4] have explained it by saying that SrO(g) vaporized from an alumina Knudsen cell, thus leading to the formation of a compound, $(\mathrm{SrO})_{1-4}\mathrm{Al_2O_3}$ in the condensed phase: they derived $D_0^\circ(\mathrm{SrO})=105$ kcal/mol by adding the heat of the formation of the $\mathrm{SrO\cdot Al_2O_3}$ compound, -19 kcal/mol, to the value obtained by Porter *et al.* However, it is less easy to explain the low value calculated from the data for all the gas-phase reactions of Eq. (21), since this equilibrium should be independent of the solid-phase composition.

TABLE 1. SUMMARY OF THE VALUES OF D_0°(SrO), kcal/mol

Method	D_0°(SrO)	Ref.
Mass spectrometry(Langmuir)	96.2±0.9[a] 102 ±5[b]	This work
Mass spectrometry(Knudsen)	102 ±5[a]	4
Mass spectrometry(Knudsen)	92.2±6[a]	22
Mass spectrometry(Knudsen)	83.6±5[a]	7
Total vapor pressure(Langmuir)	110.4±3.5[c]	23
Spectrometry	111 ±3	24
Spectrometry	94.7±1.4	25
Spectrometry	99	26
Spectrometry	106	27
Spectrometry	120	28
Theory	102 ±10[d]	29
Theory	59[e] 43[f]	30

a) Third law treatment.
b) Second law treatment.
c) Calculation from the data of Ref. 8.
d) Ion model.
e) Internuclear potential function with three parameters, *i.e.*, equilibrium bond distance, force constant, and anharmonicity constant.
f) Internuclear potential function with five parameters, *i.e.*, in addition to above three parameters, vibrational-rotational coupling constant and one constant of 1.065.

As may be seen in Table 1, the values obtained by the spectrometric method[24–28] are systematically higher than those obtained by the mass-spectrometric method. This discrepancy is presumably due to the uncertainties of the measurements of the flame temperature and its gradient by the spectrometric method, and the defference in principle between the spectrometric and the thermochemical values.

The value calculated by the ionic model[29] is in fair agreement with those experimental determined, whereas the values obtained by the internuclear potential functions[30] deviate markedly from the other values.

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