Lawrence Berkeley National Laboratory

Recent Work

Title

CONSTITUTION OF THE VAPOR AND VAPOR PRESSURE OF SrO

Permalink

<https://escholarship.org/uc/item/4jr4d3xg>

Authors

Brewer, L.
Drowart, J.

Publication Date

1959-04-01

UNIVERSITY OF
CALIFORNIA
Ernest O. Lawrence
Radiation
Laboratory

CONSTRUCTION OF THE VAPOR
AND VAPOR PRESSURE OF SrO

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract NO. W-7405-eng-48

3

CONSTITUTION OF THE VAPOR AND VAPOR PRESSURE OF SrO

L. Brewer and J. Drowart

April 1959

Printed for the U.S. Atomic Energy Commission

Printed in USA. Price 50 cents. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

CONSTITUTION OF THE VAPOR AND VAPOR PRESSURE OF SrO

L. Brewer and J. Drowart¹

Lawrence Radiation Laboratory and Department of Chemistry
University of California, Berkeley 4, California

April 1959

ABSTRACT

The high temperature vaporization data of SrO have been reviewed. It is concluded that SrO vaporizes mainly to the elements under neutral conditions. The dissociation energy of the gaseous SrO molecule is 82 ± 5 kcal/mole.

¹Department of Physics, University of Chicago, Chicago, Illinois, on leave of absence from Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, Brussels, Belgium

CONSTITUTION OF THE VAPOR AND VAPOR PRESSURE OF SrO

L. Brewer and J. Drowart

Lawrence Radiation Laboratory and Department of Chemistry
University of California, Berkeley 4, California

April 1959

Claassen and Veenemans,¹ and Moore, Allison and Struthers,² studied the sublimation of SrO coatings on Pt supports under Langmuir conditions, using gravimetric,^{1,2} polarographic² and radioactive tracer² techniques to determine the amount of SrO evaporated. The heat of sublimation obtained from the experimental data using the second law is 140 kcal/mole for the first authors and 116 kcal/mole for the latter. The weight losses however, are in good agreement. Moore, Allison and Struthers calculated from thermodynamic data for solid SrO that the free elements might represent as much as 40% of their vapor. They concluded, however, on the basis of spectroscopic data for the molecule SrO, obtained by Mahla,³ that this molecule was the more likely gaseous product. Drummond and Barrow,⁴ also assuming the main gaseous species to be SrO, showed the dissociation energy obtained from these data to be in agreement with the dissociation energy obtained by Huldt and Lagerqvist⁵ by measuring concentrations of Sr and SrO in acetylene-air flames. This value, 111 ± 4 kcal/mole, however, does not agree with spectroscopic data, which lead to a much lower dissociation energy, as pointed out by Huldt and Lagerqvist,⁵ Brewer and Mastick,⁶ and Drummond and Barrow.⁴

Thus, on comparing the various available pressure, thermodynamic and spectroscopic data, Brewer⁷ concluded that the composition of the saturated vapor of SrO was somewhat uncertain.

Several mass spectrometric investigations⁸⁻¹² of the gaseous species over SrO indicate in fact that the elements are the main products. Although carried out under different conditions, the investigations¹⁰⁻¹² agree that ionization efficiency curves, corrected for thermal ionization^{10,11} if necessary, show Sr^+ to be a primary ion produced by ionization of atomic Sr and not a fragment ion produced from SrO. Of these mass spectrometric studies, the first four⁸⁻¹¹ employed

Langmuir conditions using SrO formed from SrCO_3 coated on Pt supports, as done in the previously described Langmuir experiments.^{1,2} These studies show that thermally ionized Sr^+ ions are a minor cause for the transport of Sr. The heat of sublimation of Sr from SrO is reported to be 144,⁹ 137¹⁰ and 138¹¹ kcal/mole. In two of these mass spectrometric investigations,^{10,11} a transition point is observed around 1600°K. Since heat content measurements¹³ cover only the range 298 to 1267°K, it is difficult to explain the nature of this transition. The mass spectrometric investigation by Porter, Chupka and Inghram¹² was carried out under Knudsen conditions, using alumina as a container for SrO. The SrO pressure was measured to be about 0.3% of the Sr pressure. The ratio of orifice to vaporizing area in these measurements was smaller than 0.01. Consequently, a condensation coefficient of about 0.5 measured by Morgulis, Gavriluk and Kulik¹⁴ will not affect the equilibrium within the Knudsen cell.*

On reviewing the different results discussed above, Brewer and Searcy¹⁵ concluded that higher weight should be given to the mass spectrometric results and SrO considered to vaporize mainly to the elements.

To verify whether the total pressure measurements and the mass spectrometric results can be reconciled, the Sr pressure over SrO was again calculated here from available thermodynamic data. The free energy functions for solid and gaseous Sr, as well as for oxygen, were taken from Stull and Sinke,¹⁶ while the free energy function of solid SrO was calculated from data given by Coughlin.¹⁷

The reactions considered are

for which the heats are obtained from the heat of formation of SrO,¹⁷ the heat of sublimation of Sr¹⁶ and the dissociation energy of oxygen.¹⁶

The calculations were carried out for the constant boiling mixture, where

$$p_{\text{Sr}} = 2p_{\text{O}_2} \sqrt{87.63/32} + p_{\text{O}} \sqrt{87.63/16}$$

*Morgulis, Gavriluk and Kulik presumed their beam to consist mainly of SrO molecules, but this will not affect their conclusions.

and lead to the data summarized in table I. The free energy function corresponds to the reaction producing $\frac{1}{2}\text{O}_2(\text{g})$.

TABLE I - SrO Vapor Pressures

T	$-\Delta(F^\circ - H_{298}^\circ T)$	$-\log K_P$	$-\log P_{\text{Sr}}$	$-\log P_{\text{O}_2}$	$-\log P_{\text{O}}$
oK	cal/deg/mole		atm	atm	atm
1250	48.0	20.74	13.74	14.52	14.44
1500	47.2	15.94	10.34	11.20	10.99
2000	45.9	9.65	6.12	7.06	6.70

Partial Sr pressures were recalculated from the total weight losses given by Claassen and Veenemans,¹ and Moore, Allison and Struthers,² assuming Sr, O and O_2 to be the predominant gaseous species.

More recent measurements¹⁸ of the Sr transferred from nickel coated with a triple (Ba Sr Ca) oxide prepared from a mixture of the corresponding carbonates are markedly higher than those of Claassen and Veenemans, and Moore, Allison and Struthers and have not been included.*

The Sr pressure given by Porter, Schissel and Inghram¹¹ was also recalculated, assuming the relative ionization cross sections of Ag: Sr: SrO: O_2 : O to be 34.8: 64.3: 67.6: 6.6: 3.3 at 50 ev, as given by Otvos and Stevenson.²¹ The relative efficiency²¹ of secondary electron production on the first electrode of the electron multiplier, corrected for molecular effects²³ was taken as 1.5, 1.1, 1.1 and 1 for O_2 , Sr, SrO and Ag respectively.

*The authors¹⁸ mention that the coating material was transferred at a greater rate during the initial part of the experiments. Incomplete decomposition of the carbonates would not seem to explain this observation, as Lander¹³ has shown that the addition of SrCO_3 to BaCO_3 permits quantitative conversion of the latter carbonate to the oxide. SrO can not be reduced by Ni with formation of NiO; possible BaO - NiO phases¹⁹ and other (BaNi) oxides²⁰ are not likely to change this conclusion. If the "high purity" nickel used by Leverton and Shepherd¹⁸ does not contain Si, Mg, C or other impurities, reduction of SrO by these elements can also not be the cause of the enhanced Sr transfer. The most likely explanation thus seems reduction by carbon or gaseous carbon-hydrogen-oxygen decomposition products of the nitrocellulose binder used to coat the nickel with SrCO_3 . Weight is given to this explanation by the observation of such products and their behavior by Plumlee and Smith⁸ when studying the evaporation of BaO and SrO from Ni in a mass spectrometer

The recalculated experimental pressures are compared with the calculated ones in Fig. I. The pressures calculated from the weight transfer measurements^{1,2} are seen to be high by approximately a factor of 2, which is within the error limit of the calculated values. Such a factor would result if the measured temperatures were low by 25° compared to the thermodynamic scale, which is not unlikely in view of the fact that surface temperatures were measured. The pressure recalculated from the results of Porter, Schissel and Inghram is also in agreement with the calculated value.

On the basis of this agreement between calculated and measured values and the different mass spectrometric observations that gaseous Sr is more important than SrO, it seems clear that atomic Sr and atomic and molecular oxygen are the predominant species over solid SrO under neutral conditions.

Dissociation Energy of the SrO Molecule

In the spectroscopic determination of this dissociation energy, there is, in addition to the inherent uncertainty of the Birge Sponer extrapolation, considerable uncertainty as to the identification of the electronic ground state of the SrO molecule.²⁴

Thermochemical calculations based on partial pressure measurements in flames^{5,25} are uncertain. In these measurements a known amount of the metal is injected in an air-acetylene flame and the concentration of free Sr atoms measured. The deficit in Sr atoms is then assumed to be present as SrO molecules. It is, however, possible^{26,27} that gaseous hydroxides or other molecules contribute in removing Sr atoms.²⁸

Thermochemical calculations based on the ratios of Sr^+/SrO^+ ion intensities can be carried out only for the data reported by Porter, Chupka and Inghram. The latter authors report a ratio of Sr^+/SrO^+ of 300 at 2100°K under equilibrium conditions, using 50 ev electrons, the O_2 pressure calculated from their data being 2.4×10^{-6} atm.

The reported ratios Sr^+/SrO^+ , obtained with ionizing electrons of comparable energy are fairly consistent for the various Langmuir experiments, but appreciably lower than under Knudsen conditions. Aldrich⁹ reports 34 at 1725°K and 21 at 1810°K and Pelchowitch about 75 at 1690°K (using 50 ev electrons) and from 200 at 1575° to 50 at 1750°K. Bickel and Holroyd report that the ratio decreases with time from about 10 to 100, the temperature range being 1600-1800°K. These ratios can be reconciled with the ratios obtained under equilibrium conditions if it is assumed that oxidizing conditions, maybe

due to CO_2 resulting from incomplete decomposition of the carbonate, prevail in the Langmuir experiments. The time dependence observed by Bickel and Holroyd may well be indicative of this fact as well as the high ratio of oxygen to Sr intensities reported by the latter authors. From the data given by Porter, Chupka and Inghram, using the relative cross sections given earlier, one calculates the pressures:

$$p_{\text{Sr}} = 2.8 \times 10^{-6} \text{ atm}$$

$$p_{\text{O}_2} = 2.4 \times 10^{-6} \text{ atm}$$

$$p_{\text{SrO}} = 8.7 \times 10^{-9} \text{ atm}$$

To calculate the dissociation energy $D_{298}^{\circ}(\text{SrO})$, the free energy function of the gaseous SrO molecule was calculated using the vibration frequency and interatomic distance measured by Almkvist and Lagerqvist²⁴ for a $^1\Sigma$ state which may not be the ground state. In the absence of accurate spectroscopic data, the electronic partition function was taken as unity. With $-(F^{\circ} - H_{298}^{\circ}/T) = 64.1 \text{ cal/deg/mole}$ for gaseous SrO at 2100°K , one calculates from the above mentioned pressures $D_{298}^{\circ}(\text{SrO}) = 80 \pm 5 \text{ kcal/mole}$, close to the value of $83.6 \pm 5 \text{ kcal/mole}$ obtained by Porter, Chupka and Inghram, who used a quantum weight of 3 for the electronic ground state. The agreement results from a partial compensation of the lower SrO pressure calculated here by the lower multiplicity used here.

The reported heats of sublimation of Sr^9 and SrO^{10} obtained from 2nd law measurements are too uncertain to warrant a calculation of the SrO dissociation energy.

The best available dissociation energy of SrO, assuming a $^1\Sigma$ state, is thus $81 \pm 5 \text{ kcal/mole}$.

REFERENCES

- 1) A. Claassen and C. F. Veenemans, Z. Physik 80, 342 (1933).
- 2) Moore, Allison and Struthers, J. Chem. Phys. 18, 1572 (1950).
- 3) K. Mahla, Z. Physik 81, 625 (1933).
- 4) G. Drummond and R. F. Barrow, Trans. Faraday Soc. 47, 1275 (1951).
- 5) L. Huldt and A. Lagerqvist, Ark. Fys. 2, 333 (1950).
- 6) L. Brewer and D. F. Mastick, J. Am. Chem. Soc. 73, 2045 (1951).
- 7) L. Brewer, Chem. Rev. 52, 1 (1953).
- 8) R. H. Plumlee and L. P. Smith, J. Appl. Phys. 21, 811 (1950).
- 9) L. T. Aldrich, J. Appl. Phys. 22, 1168 (1951).
- 10) I. Pelchowitch, Phillips Research Reports 9, 42 (1954).
- 11) P. W. Bickel and L. V. Holroyd, J. Chem. Phys. 22, 1793 (1954).
- 12) Porter, Chupka and Inghram, J. Chem. Phys. 23, 1347 (1955).
- 13) J. J. Lander, J. Am. Chem. Soc. 73, 5794 (1951).
- 14) Morgulis, Gavriljuk and Kulik, Doklady Akad Nauk SSSR 101, 479 (1955).
- 15) L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem. 7, 259 (1956).
- 16) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements,"
Advances in Chemistry Series 18, American Chemical Society, Washington, 1957.
- 17) J. P. Coughlin, Bureau of Mines Bull 542 (1955).
- 18) W. F. Leverton and W. G. Shepherd, J. Appl. Phys. 23, 787 (1952).
- 19) J. J. Lander, J. Am. Chem. Soc. 73, 2450 (1951).
- 20) J. J. Lander and L. A. Wooten, J. Am. Chem. Soc. 73, 2452 (1951).
- 21) J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 546 (1956).
- 22) Inghram, Hayden and Hess, Nat. Bur. Stand. (U.S.) Circular 522, 257 (1953).
- 23) Stanton, Chupka and Inghram, Rev. Sci. Instr. 27, 109 (1956).
- 24) G. Almkvist and A. Lagerqvist, Ark. Fys. 1, 477 (1949).
G. Almkvist and A. Lagerqvist, Ark. Fys. 2, 233 (1950).
A. Lagerqvist, Ark. Fys. 8, 83 (1954).
A. Lagerqvist and L. Huldt, Ark. Fys. 8, 427 (1954).
L. Huldt and A. Lagerqvist, Ark. Fys. 9, 227 (1955).
- 25) A. Lagerqvist and L. Huldt, Z. Naturforsch. 9a, 991 (1954).
- 26) G. G. James and T. M. Sugden, Nature 175, 333 (1955).
- 27) A. Lagerqvist and L. Huldt, Naturwissenschaften 42, 365 (1955).
L. Huldt and E. Knoll, Ark. Fys. 11, 229 (1956).
L. Huldt and A. Lagerqvist, Ark. Fys. 11, 356 (1956).
- 28) A. G. Gaydon, Mem. soc. roy. sci. Liège 18, 507-12 (1957).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.