MASTER

HIGH TEMPERATURE CHEMISTRY -
FUNDAMENTALS OF EFFUSION AND THERMODYNAMICS OF MATERIALS

FINAL REPORT

31 August 1971

Covering the period from 1 June 1961 through 31 August 1971.

To:

Division of Research
U. S. Atomic Energy Commission

Contract No. At(11-1)-1029

From:

The Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Principal Investigator:

Phillip G. Wahlbeck
Associate Professor of Chemistry
Department of Chemistry

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High Temperature Chemistry - Fundamentals of Effusion
and Thermodynamics of Materials

Phillip G. Wahlbeck
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

FINAL REPORT

I. ACKNOWLEDGMENT

The personnel associated with this project in the past and at the present and the Illinois Institute of Technology wish to thank the U. S. Atomic Energy Commission for their support of the research summarized in this document.

This Final Report summarizes work supported by the U. S. Atomic Energy Commission under contract number AT(11-1)-1029 from 1 June 1961 through 31 August 1971. The subjects which have been studied are: (1) effusion of gases through orifices, (2) thermodynamics of selected chemical systems, and (3) gas-surface interactions.

II. SCIENTISTS WHO HAVE RECEIVED DEGREES UNDER THIS PROGRAM

Ph. D.

Name, Date when Ph. D. was Received, Present Position

- a. L. N. Yannopoulos, 1963, Westinghouse Corp., Pittsburgh, Pennsylvania.
- b. M. L. Lieberman, 1965, Sandia Corp., Albuquerque, New Mexico.
- c. G. J. Macur, 1965, IBM, Endicott, New York.
- d. Akio Suzuki, 1966, Sumitomo Chemical Company, Niihama, Ehime, Japan.
- e. K. C. Wang, 1966, Ceramtec Industries, Inc., Chicago, Illinois.
- f. P. Budininkas, 1967, General American Transportation Corporation, Chicago, Illinois.
- g. E. N. Sloth, 1969, stock broker.
- h. B. D. Holt, 1969, Argonne National Laboratory, Argonne, Illinois.
- i. S. J. Wey, 1971, University of Missouri - Rolla, Rolla, Missouri (post doctoral position, 1 September 1971).

M. S.

Name, Date when M. S. was Received, Present Position

- a. R. L. Wagner, 1965, Oak Ridge National Laboratory.
- b. H. J. Leary, Jr., 1968, (received Ph. D., 1971, University of Iowa, adviser E. D. Cater), General Electric Co., Schenectady, New York.
- c. A. Liakus, 1970, graduate student, University of Nebraska.

III. CURRENT STUDENTS IN HIGH TEMPERATURE SCIENCE AT IIT

- a. Robert Ni, Ph. D. candidate, third stage student
- b. Hung Yuan Wu, Ph. D. candidate, third stage student
- c. Leo W. Huang, Ph. D. candidate, third stage student
- d. Bill C. Mikuska, Ph. D. candidate, second stage student
- e. Ming Biann Liu, Ph. D. candidate, second stage student

IV. BIOGRAPHICAL SKETCH OF PRINCIPAL INVESTIGATOR

Name: Phillip Glenn Wahlbeck

Birth: March 29, 1933

Kankakee, Illinois

Education:

B. S., Chemistry, 1954, University of Illinois, Urbana, Illinois

Ph. D., Physical Chemistry, 1958, University of Illinois,
Urbana, Illinois

Research Director: Professor T. E. Phipps

Thesis: "Observations on Molecular Effusion IV."

Post-doctoral Research Associate, 1958-60

University of Kansas, Lawrence, Kansas

Research Director: Professor Paul W. Gilles

Research: Ti-O System

Academic Experience:

Instructor: 1960-61, Illinois Institute of Technology

Assistant Professor: 1961-67, Illinois Institute of Technology

Associate Professor: 1967- present, Illinois Institute of
Technology

Other Experience:

Administrative Officer, 1967-68, Department of Chemistry,
Illinois Institute of Technology

Gjesteprofessor, 1970, Institutt for uorganisk kjemi,
Norges tekniske høgskole, Trondheim, Norway

V. RESEARCH COMPLETEDA. Publication List - chronological

1. L. N. Yannopoulos, R. K. Edwards, and P. G. Wahlbeck, "The Thermodynamics of the Yttrium-Hydrogen System," J. Phys. Chem., 69 [8], 2510-5 (1965).
2. M. L. Lieberman and P. G. Wahlbeck, "The Thermodynamics of the Scandium-Hydrogen System," J. Phys. Chem., 69, [10], 3514-9 (1965).
3. M. L. Lieberman and P. G. Wahlbeck, "The Scandium-Yttrium-Hydrogen System," J. Phys. Chem., 69 [11], 3973-80 (1965).
4. Akio Suzuki and P. G. Wahlbeck, "Vaporization Study of the Titanium Tellurium System," J. Phys. Chem., 70 [6], 1914-23 (1966).
5. G. J. Macur, R. K. Edwards, and P. G. Wahlbeck, "Multiple Knudsen Cell Effusion. Enthalpies of Vaporization of Indium and Gallium," J. Phys. Chem., 70 [9], 2956-65 (1966).
6. Akio Suzuki and P. G. Wahlbeck, "Gaseous Products from Vaporization of Titanium Selenides," Trans. Met. Soc. AIME, 236 [9], 1375-7 (1966).
7. Phillip G. Wahlbeck and Paul W. Gilles, "The Dissociation Energy of TiO(g) and the High Temperature Vaporization and Thermodynamics of the Titanium Oxides. II. Trititanium Pentoxide," J. Chem. Phys., 46, 2465 (1967).
8. K. C. Wang and P. G. Wahlbeck, "Effusion I. Angular Number Distributions of Gaseous CsCl from a Near-Ideal Orifice into Vacuum," J. Chem. Phys., 47 [11], 4799-4809 (1967).
9. G. J. Macur, R. K. Edwards, and P. G. Wahlbeck, "Measurement of Activities in Gallium-Indium Liquid Alloys," J. Phys. Chem., 72

- [3], 1047-1050 (1968).
10. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules. I. Sulfur," J. Chem. Phys. 48, 2859-2866 (1968).
 11. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules. II. Selenium," J. Chem. Phys. 48, 2867-2869 (1968).
 12. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules. III. Tellurium," J. Chem. Phys. 48, 2870-2873 (1968).
 13. P. G. Wahlbeck and T. E. Phipps, "Effusion II. Angular Number Distributions of Gaseous Cadmium from a Right-Circular Cylindrical Orifice into Vacuum," J. Chem. Phys. 49, 1603-1608 (1968).
 14. J. Q. Adams, T. W. Phipps, and P. G. Wahlbeck, "Effusion III. Angular Number Distributions of Gaseous CsCl from Right-Circular Cylindrical Orifices into Vacuum," J. Chem. Phys. 49, 1609-1616 (1968).
 15. K. C. Wang and P. G. Wahlbeck, "Effusion IV. Angular Number Distributions of Gaseous CsCl from Right-Circular Cylindrical Orifices into Vacuum," J. Chem. Phys. 49, 1617-1625 (1968).
 16. Paul W. Gilles, Peter J. Hampson and Phillip G. Wahlbeck, "Dissociation Energy of TiO(g) and the High-Temperature Vaporization and Thermodynamics of the Titanium Oxides. V," J. Chem. Phys. 50, 1048-1049 (1969).
 17. Herbert J. Leary, Jr. and P. G. Wahlbeck, "The Vaporization Process and Rate of Effusion of Crystalline Sc_2Se_3 ," High Temp.

- Sci., 1, 277-286 (1969).
18. J. Q. Adams, T. E. Phipps, and P. G. Wahlbeck, "Effusion V. Angular Number Distributions of Gaseous CsCl from Conical Orifice into Vacuum," J. Chem. Phys., 51, 920-923 (1969).
 19. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Erratum: Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules. II. Selenium; III. Tellurium," J. Chem. Phys. 51, 1686 (1969).
 20. Robert C. Mellucci and P. G. Wahlbeck, "Mass Spectrometric Observations of Gaseous Boron Selenides," Inorg. Chem. 9, 1065-8 (1970); see Appendix 1.
 21. K. C. Wang and P. G. Wahlbeck, "Effusion VI. Velocity Distributions of Gaseous CsCl from Near-Ideal and Right Circular Cylindrical Orifices," J. Chem. Phys. 53, 2896-2905 (1970); see Appendix 2.
 22. P. G. Wahlbeck, "Effusion VII. The Failure of Isotropy of a Gas in an Effusion Cell and the Transition Region," J. Chem. Phys. (accepted for publication); see Appendix 3.
 23. Song Jey Wey and P. G. Wahlbeck, "Effusion VIII. Orifice Transmission Probabilities as a Function of Pressure for a Near-Ideal and for Right-Circular Cylindrical Orifices," J. Chem. Phys. (accepted for publication); see Appendix 4.
 24. Hung Yuan Wu and P. G. Wahlbeck, "Vapor Pressures and the Standard Enthalpy Change for Sublimation of Ti(s, β)," High Temp. Sci. (submitted); see Appendix 5.

B. Publication List - Classified by Subjects

(Some papers dealing with more than one subject are listed twice.)

EFFUSION

1. K. C. Wang and P. G. Wahlbeck, "Effusion I. Angular Number Distributions of Gaseous CsCl from a Near-Ideal Orifice into Vacuum," J. Chem. Phys., 47, 4799-4809 (1967).
2. P. G. Wahlbeck and T. E. Phipps, "Effusion II. Angular Number Distributions of Gaseous Cadmium from a Right-Circular Cylindrical Orifice into Vacuum," J. Chem. Phys., 49, 1603-8 (1968).
3. J. Q. Adams, T. E. Phipps, and P. G. Wahlbeck, "Effusion III. Angular Number Distributions of Gaseous CsCl from Right-Circular Cylindrical Orifices into Vacuum," J. Chem. Phys., 49, 1609-17 (1968).
4. K. C. Wang and P. G. Wahlbeck, "Effusion IV. Angular Number Distributions of Gaseous CsCl from Right-Circular Cylindrical Orifices into Vacuum," J. Chem. Phys. 49, 1617-25 (1968).
5. J. Q. Adams, T. E. Phipps, and P. G. Wahlbeck, "Effusion V. Angular Number Distributions of Gaseous CsCl from a Conical Orifice into Vacuum," J. Chem. Phys., 51, 920-3 (1969).
6. K. C. Wang and P. G. Wahlbeck, "Effusion VI. Velocity Distributions of Gaseous CsCl from Near-Ideal and Right-Circular Cylindrical Orifices," J. Chem. Phys. 53, 2896-2905 (1970); see Appendix 2.
7. P. G. Wahlbeck, "Effusion VII. The Failure of Isotropy of a Gas in an Effusion Cell and the Transition Region," J. Chem. Phys. (accepted for publication); see Appendix 3.

8. Song Jey Wey and P. G. Wahlbeck, "Effusion. VIII. Orifice Transmission Probabilities as a Function of Pressure for a Near-Ideal and for Right-Circular Cylindrical Orifices," J. Chem. Phys. (accepted for publication); see Appendix 4.
9. G. J. Macur, R. K. Edwards, and P. G. Wahlbeck, "Multiple Knudsen Cell Effusion. Enthalpies of Vaporization of Indium and Gallium," J. Phys. Chem., 70, 2956-65 (1966).

DISSOCIATION ENERGIES OF GASEOUS MOLECULES

1. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules. I. Sulfur," J. Chem. Phys., 48, 2859-66 (1968).
2. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules II. Selenium," J. Chem. Phys., 48, 2867-9 (1968).
3. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules III. Tellurium," J. Chem. Phys., 48, 2870-3 (1968).
4. P. Budininkas, R. K. Edwards, and P. G. Wahlbeck, "Erratum: Dissociation Energies of Group VIA Gaseous Homonuclear Diatomic Molecules. II. Selenium; III. Tellurium," J. Chem. Phys., 51, 1686 (1969).
5. Phillip G. Wahlbeck and Paul W. Gilles, "Dissociation Energy of TiO(g) and the High-Temperature Vaporization and Thermodynamics of the Titanium Oxides. II. Trititanium Pentoxide," J. Chem. Phys., 46, 2465-2473 (1967).
6. Paul W. Gilles, Peter J. Hampson, and Phillip G. Wahlbeck, "Dis-

sociation Energy of TiO(g) and the High-Temperature Vaporization and Thermodynamics of the Titanium Oxides. V," J. Chem. Phys., 50, 1048-9 (1969).

METAL-HYDROGEN SYSTEMS

1. L. N. Yannopoulos, R. K. Edwards, and P. G. Wahlbeck, "The Thermodynamics of the Yttrium-Hydrogen System," J. Phys. Chem., 69, 2510-5 (1965).
2. M. L. Lieberman and P. G. Wahlbeck, "The Thermodynamics of the Scandium-Hydrogen System," J. Phys. Chem., 69, 3514-9 (1965).
3. M. L. Lieberman and P. G. Wahlbeck, "The Scandium-Yttrium-Hydrogen System," J. Phys. Chem., 69, 3973-80 (1965).

ELEMENTS-THERMODYNAMICS

1. G. J. Macur, R. K. Edwards, and P. G. Wahlbeck, "Multiple Knudsen Cell Effusion. Enthalpies of Vaporization of Indium and Gallium," J. Phys. Chem., 70, 2956-65 (1966).
2. Hung Yuan Wu and P. G. Wahlbeck, "Vapor Pressures and the Standard Enthalpy Change for Sublimation of $\text{Ti(s,}\beta\text{)}$," High Temp. Sci. (submitted); see Appendix 5.

LIQUID METAL SOLUTIONS

1. G. J. Macur, R. K. Edwards, and P. G. Wahlbeck, "Measurement of Activities in Gallium-Indium Liquid Alloys," J. Phys. Chem., 72, 1047-1050 (1968).

MASS SPECTROMETRIC STUDIES

1. Akio Suzuki and P. G. Wahlbeck, "Gaseous Products from Vaporization of Titanium Selenides," Trans. Met. Soc. AIME, 236, 1375-7 (1966).

2. Robert C. Melucci and P. G. Wahlbeck, "Mass Spectrometric Observations of Gaseous Boron Selenides," *Inorg. Chem.* 9, 1065-8 (1970); See Appendix 1.
3. Akio Suzuki and P. G. Wahlbeck, "Vaporization Study of the Titanium-Tellurium System," *J. Phys. Chem.*, 70, 1914-23 (1966):
4. Herbert J. Leary, Jr. and P. G. Wahlbeck, "The Vaporization Process and Rate of Effusion of Crystalline Sc_2Se_3 ," *High Temp. Sci.*, 1, 277-286 (1969).

VI. RESEARCH IN PROGRESS

The work reported in this section are studies which have not yet reached completion. Research on these problems will be continued; the results reported here are to be considered tentative.

A. Values of D_0°

1. ScSe(g), YSe(g), and LaSe(g) (Robert Ni)

The dissociation energy of a gaseous diatomic molecule is the energy change or enthalpy change at 0°K for the standard state process given by

To the chemist these values are of interest because they indicate the strength of bonds between the atoms in forming the molecules; such values can be correlated with quantum mechanical principles and calculations related to bonding. To the thermodynamicist these values permit one to calculate equilibrium constants for any reactions involving the molecule and other species for which data are known.

There is a considerable amount of data presently available regarding the dissociation energies of oxides and sulfides. The data on selenides is less abundant, and the data on tellurides even more sketchy.

The above facts led us toward studies of transition metal selenides. In this section are reported results obtained from a mass spectrometric study of ScSe(g), YSe(g), and LaSe(g).

Samples.- In the experiments reported in this study, samples of crystalline scandium, yttrium, and lanthanum selenides were utilized. These samples were prepared by direct means by heating stoichiometric amounts of elements. The weighed mixtures of the elements were placed in quartz

ampules. In the cases of scandium and yttrium selenides, an inner alumina crucible was used also. The ampules were evacuated to 10^{-5} torr and sealed. The samples were heated according to the following schedules: scandium and yttrium selenides, 800°C for 48 hours followed by 1000°C for 12 hours; lanthanum selenides, 500°C for 6 days.

Scandium metal was obtained by preparation from Sc_2O_3 , obtained from the American Scandium Corporation, by reduction at the Ames Laboratory of Iowa State University. An analysis of the metal by the Ames Laboratory showed the following impurities: O, 1805 p.p.m.; N, 80 p.p.m.; H, 15 p.p.m.; Y, 0.03%; Er, < 0.01%; Tm, < 0.01%; Yb, < 0.004%; Lu, < 0.01%; Si, 80 p.p.m.; Ca, 320 p.p.m.; Fe, 180 p.p.m.; and Ta, 1000 p.p.m.

Yttrium metal was obtained from the Lindsay Chemical Division of American Potash and Chemical Corporation with a purity designation of 99.9%.

Lanthanum metal was purchased in the form of turnings from Bernard Ring, Incorporated, New York, New York. The stated purity was 99.9% with Ce, 0.02%; Pr, 0.02%; and Nd, 0.003%. The turnings have been protected from oxidation by submersion in a heavy oil. To remove the oil, the turnings were washed several times with reagent grade benzene in an Ar-filled dry box.

Selenium was obtained from the American Smelting and Refining Company, South Plainfield, New Jersey, and had a stated purity of 99.999+%. The impurities were Te, Cu, As, and Si in amounts less than 0.0001% each.

Silver metal was used in a calibration procedure in the mass spectrometric measurements. The silver was spectroscopically standardized grade from Johnson, Matthey and Company, Limited. The elements Bi, Ca, Fe,

and Mg were reported to be present in amounts less than one p.p.m.

Mass Spectrometry.- Vapor species in equilibrium with these systems were analysed with a Bendix Corporation time-of-flight mass spectrometer, model number 12-107. This mass spectrometer was equipped so that oscilloscopic observations of the mass spectrum could be made or so that ion intensities could be recorded with a Leeds and Northrup recorder.

High Temperature Knudsen Cell Source.- The equilibrium vapor species entered the ion source of the mass spectrometer without any surface collisions from a Knudsen cell high temperature source based on the design by Chupka and Inghram.¹ A tungsten effusion cell, heated by electron bombardment, was surrounded by two Ta radiation shields. Outside the radiation shields, ion deflection plates were placed so that ions originating from the Knudsen cell and shields area could be removed. The molecular beam could be shuttered to prevent its entrance into the ion source of the mass spectrometer. The temperature of the effusion cell was measured by sighting a disappearing filament optical pyrometer through a window and prism, through the ion source, and onto the Knudsen cell orifice.

The Knudsen effusion cells were fabricated from swaged W rod with tungsten carbide tools. Table I describes the orifice dimensions of the different effusion cells which were used in the studies which are indicated in Table I.

The electron bombardment power supply was regulated so that the emission current from a hot tungsten filament surrounding the filament was constant. The temperature of the effusion cell was quite constant so that there was no perceptable change in ion intensities over long periods of time.

The optical pyrometer used in these studies was calibrated by

sighting (using the low temperature scale) on a black-body cavity at the temperature of the melting point of Cu using a sample from the National Bureau of Standards. The intermediate temperature scale was calibrated through comparison of temperature readings on the low and intermediate scales when sightings were made on a heated lamp filament. A correction for the reflection of radiant energy by the window and prism was calculated from measurements of the apparent temperature of an object with and without the window-prism assembly.

The relation between the pressure of a species in the Knudsen cell, P_i , and its ion intensity, I_i^+ , is

$$P_i = K \frac{I_i^+ T}{Q_i \eta_i F_i}, \quad (1)$$

where T is the absolute temperature, Q_i is the ionization cross section, η_i is the multiplier gain, F_i is the isotopic fraction for the species, and K is a proportionality constant. For different species, the ion intensities are all measured at the same ionizing electron energy above the ions' appearance potential. One may make use of the usual effusion equation

$$G_i = \frac{P_i A t \sqrt{M_i}}{\sqrt{2\pi R T}}, \quad (2)$$

where G_i is the mass of the species which effuses for which the molecular weight is M_i through an orifice with an effective area A in time t . Eliminating P_i in equation (2) by substitution of equation (1) yields

$$G_i = \frac{K I_i^+ T A t \sqrt{M_i}}{Q_i \eta_i F_i \sqrt{2\pi R T}}. \quad (3)$$

In order to determine the value of the constant K in equation (1), a calibration procedure was performed which made use of equation (3) in which the entirety of a Ag sample, which had been weighed on a balance, was allowed to effuse from the Knudsen cell. The values of the calibration constant are also given in Table I.

Comments on Data Handling.- The mass spectrometric data have been handled in several ways which are described in the following paragraphs.

To identify the ions emitted from the ion source, mass scans have been run at a constant ionizing electron voltage of 50 eV. Peaks were observed in the mass spectrum at mass to charge ratios for the ions. The value of the mass to charge ratio, isotopic distributions, and shutter effects aid one in identifying the species.

In order to identify the parent species which gave rise to the ions, ionization efficiency data are acquired; i.e., intensity vs. ionizing electron voltage for ions of a given mass to charge ratio. Values of the appearance potential and shapes of the ionization efficiency curves aid in identifying the parent species.

Thermodynamic data have been acquired for particular reactions by measuring the temperature dependence of the ion intensities at 5 eV. above the appearance potential. The experiments were performed so that a set of I_i^+ and T data were collected at one given mass, the mass selector changed to a new mass, a new set of data collected for a new mass, etc. A least squares line was determined for the set of data. When such lines have been determined for all species in the reaction, a third-law treatment, in conjunction with use of Ag calibration data, has been performed on the data.

To perform the thermodynamic calculations, values of $(G_T^\circ - H_0^\circ)/T$

Table I. Orifice Parameter Data

Ag Calib. No.	3	5	6	7	9
Temperature, °K	1490	1444.6	1511.4	1352.3	1429.2
Experiment	LaSe Runs 1-4	LaSe Run 5	ScSe Runs 1-2	ScSe Runs 3-5	YSe Runs 1-6
Orifice Area, square cm	0.020364	0.011079	0.0110213	0.020365	0.020106
Orifice Trans. Factor (de Marcus)	0.31	0.61	0.756	0.669	0.805
Mass Spectrometer Calib Factor	7.3141	9.2850	11.6103	21.5086	19.8480
P _{Ag, torr} (Exp't)	0.20574	0.14060	0.13592	0.02255	0.05509
P _{Ag, torr} (Calculated from Nesmeyanov's Equation)	0.22670	0.11376	0.30932	0.02427	0.08900

and $(H_T^\circ - H_0^\circ)/T$ for gaseous species have been calculated from statistical mechanical equations given by Stull.² For monatomic atoms of the elements, the electronic states with energies less than $20,000 \text{ cm}^{-1}$ have been used, using data from Moore.³ For the diatomic gaseous molecules, the molecular parameters are given in Table II and are the same values which have been used by Drowart.⁴

The dissociation energies of the metal monoselenides were determined through use of two different reactions. The first type of reaction was the dissociation reaction; i.e.,

In order to utilize this type of reaction one must know absolute pressures of the species in order to determine the equilibrium constant. The second type of reaction was the isomolecular reaction; i. e.,

In this case one does not need to know absolute pressures, but one must know the dissociation energy of NSe(g) to determine the dissociation energy of MSe(g) .

Observed Species.- In Table III are listed the observed species, the appearance potentials from this study, and previously observed appearance potentials.

The MSe^+ , M^+ , and Se^+ ions are believed to be from the parent species MSe(g) , M(g) , and Se(g) , respectively. The values of the appearance

Table II. Molecular Parameters

	ScSe(g)	YSe(g)	LaSe(g)
mass	123.92	167.87	217.87
σ	1	1	1
elec. state	2Σ	2Σ	2Σ
g_0	2.0	2.0	2.0
Term value	0	0	0
ω_e	410.00	360.00	350.00
$\omega_e x_e$	0	0	0
$\omega_e y_e$	0	0	0
B_e	0.11727	0.07237	0.05813
α_e	0	0	0
$r_e, \text{\AA}$	2.240	2.360	2.400

Table III. Observed Species

	Species	Appearance Pot, eV observed	Appearance Pot, eV literature ³
ScSe System	ScSe ⁺	7.5	—
	Sc ⁺	6.7	6.7
	Se ⁺	10.0	9.7
	HSe ⁺	—	—
	H ₂ Se ⁺	10.5	—
YSe System	YSe ⁺	7.9 ± 0.5	—
	Y ⁺	6.3 ± 0.5	6.5
	Se ⁺	9.9 ± 0.5	9.7
	HSe ⁺	—	—
	H ₂ Se ⁺	10.5	—
LaSe System	LaSe ⁺	6.0 ± 0.5	—
	La ⁺	5.5 ± 0.5	5.6
	Se ⁺	9.9 ± 0.5	9.7
	HSe ⁺	—	—
	H ₂ Se ⁺	10.5	—

potentials and smooth ionization efficiency curves do not indicate extensive fragmentation.

The source of the HSe^+ and H_2Se^+ is assumed to be from $\text{H}_2\text{Se(g)}$. The origin of $\text{H}_2\text{Se(g)}$ is probably from the chemical reaction of adsorbed H_2O and deposited Se or selenides on the Ta radiation shields. In these experiments the amount of $\text{H}_2\text{Se(g)}$ which was shuttered and appeared to be effusing from the Knudsen cell was estimated to be much less than the amount of Se(g) in the cases of the La-Se system and the Sc-Se system in which the Se(g) pressure is large. In these cases reliable values of the dissociation energy can be obtained by using the dissociation reaction. In the case of the Y-Se system, the solid compounds are so stable that the Se(g) pressure is much lower and $\text{H}_2\text{Se(g)}$ presents serious complications. The complication is caused by the fact that Se has isotopes at masses of 74, 76, 77, 78, 80, and 82 with mass 80 being the most abundant. Thus H_2^{78}Se contributes to the intensity of the peak at mass 80 also. To obtain the dissociation energy of YSe(g) , the following reaction has been used:

A measurement of the Se(g) pressure is not required in this case. Several sets of data for each of the dissociation energies have been obtained from the mass spectrometer. Thus far, the data have been analysed by the third-law method. Runs have been considered to be reliable if there is no known experimental technical flaw and if in the third-law analysis there is no temperature dependence in the values of D° greater than $1.5 \text{ kcal/200}^\circ\text{K}$.

The data presently available are summarized in Tables IV, V, and VI. In Table VII the values for D° from this study and the work of Drowart

Table IV. D° of ScSe(g)

Run	Temperature Range	D° (average)
1	1769 - 2116°K	91.26 kcal/mole
2	1829 - 2126°K	89.88 kcal/mole
4	1898 - 2113°K	88.89 kcal/mole
5	1855 - 2105°K	89.71 kcal/mole
6	1826 - 2110°K	89.00 kcal/mole
		Ave. 89.75 kcal/mole

Table V. D° of YSe(g)

Run	Temperature Range	D° (average) ^a
2 & 3	1965 - 2237°K	100.73 kcal/mole
4	1902 - 2183°K	100.57 kcal/mole
5	1867 - 2176	100.62 kcal/mole
		Ave. 100.64 kcal/mole

(a) Based on isomolecular reaction

using $D^\circ[\text{ScSe(g)}] = 89.75$.

Table VI. D° of LaSe(g)

Run	Temperature Range	D° (average)
1	1998 - 2227°K	112.84 kcal/mole
2	1980 - 2236°K	112.75 kcal/mole
3	1973 - 2210°K	113.82 kcal/mole
4	1980 - 2208°K	114.32 kcal/mole
5	1965 - 2214°K	111.89 kcal/mole
		Ave. 113.12 kcal/mole

Table VII. Values of D°

Species	D° , this laboratory	D° , Drowart <u>et al.</u> ⁴
ScSe(g)	89.75 kcal/mole	91.3 ± 3.5 kcal/mole
YSe(g)	100.64 kcal/mole	104.9 ± 3.5 kcal/mole
LaSe(g)	113.12 kcal/mole	114.3 ± 3.5 kcal/mole

et al.⁴ are given. For ScSe(g) and LaSe(g) the values from both groups are in good agreement. For YSe(g) we believe that our value fits the trends in the D° values better than the value by Drowart et al.⁴

The trend in the dissociation energies of these selenide molecules is such that LaSe(g) is the most stable (largest value for D°) with YSe(g) and ScSe(g) following with lower stabilities. This trend is exactly the same as that which was observed for LaO(g), YO(g) and ScO(g) and for LaS(g), YS(g), and ScS(g).

With variations of the oxygen family member with a given metal, the trend is that MO(g) is more stable than MS(g), and MS(g) is more stable than MSe(g).

To fully understand the nature of the effects causing these trends, it will be necessary that quantum mechanical calculations be pressed further. At the present time, the trend in the dissociation energies with changing oxygen family members is expected because of the weakening of bonds caused by increasing the size of the orbitals on one of the atoms. However, with variation in metal atoms, one observes that the larger the metal atom the stronger the bond. This has not been satisfactorily explained at present.

2. TiO(g) (Hung Yuan Wu)

Values for the dissociation energy of TiO(g) range from 156.9 and 157.9 kcal mole⁻¹ determined by Drowart et al.⁵ to 167.38 kcal mole⁻¹ reported by Wahlbeck and Gilles.⁶ Drowart et al.⁵ made mass spectrometric measurements on isomolecular reactions involving several different gaseous monoxide molecules. Wahlbeck and Gilles⁶ made classical Knudsen vapor pressure measurements on congruently vaporizing $Ti_3O_5(s)$. From mass spectrometric measurements they concluded that

Recent mass spectrometric studies by Hampson and Gilles⁷ and by this group have shown that the above reaction for the congruent vaporization of $\text{Ti}_3\text{O}_5(\text{s})$ is not correct but rather

In this laboratory, a program was developed to measure $D^\circ(\text{TiO}(\text{g}))$ through analysis of another vaporization reaction. It was hoped that a correct value of the dissociation energy would be achieved.

In a paper by Gilles et al.⁸ a diagram of vapor pressure vs. composition (at fixed temperature) for the Ti-O system was presented. This diagram was drawn from available experimental data. From the diagram, one would conclude that

If this is the predominant reaction, then one could make vapor pressure measurements of $\text{TiO}(\text{g})$ in equilibrium with the two condensed phases $\text{Ti}_2\text{O}_3(\text{s})$ and $\text{Ti}_3\text{O}_5(\text{s})$. Thus, values of the equilibrium constant for this reaction can be determined; by second-law and third-law treatments of the K values at known temperatures, the value of D° can be determined.

Samples of the two phases $\text{Ti}_2\text{O}_3(\text{s})$ and $\text{Ti}_3\text{O}_5(\text{s})$ were prepared by heating stoichiometric mixtures of $\text{Ti}(\text{s})$ and $\text{TiO}_2(\text{s})$ in a W crucible at 1600°C for 40 hr. The $\text{Ti}(\text{s})$ was from a bar of "icdide" Ti with a stated purity of

99.999% obtained from the Research Organic/Inorganic Chemical Company of Sun Valley, California. The $\text{TiO}_2(\text{s})$ was "Baker Analyzed Reagent" grade material; the following analysis has been given: water soluble salts, 0.04%; Arsenic (As), 0.0001%; Iron (Fe), 0.002%; Lead (Pb), 0.006%; Zinc (Zn), 0.01%. Phases present in the prepared samples were determined through x-ray powder diffraction analysis using published data from Andersson, *et al.*⁹

The vapor in equilibrium with $\text{Ti}_2\text{O}_3(\text{s})$ and $\text{Ti}_3\text{O}_5(\text{s})$ was examined mass spectrometrically. The mass spectrometer and Knudsen cell inlet are described in Appendix 5. The vapor species observed in this study were Ti^+ , TiO^+ , and TiO_2^+ . No observation of O^+ or tungsten oxide ions was made.

Ionization efficiency curves for each species was determined. The appearance potentials are given in Table VIII. Because the appearance potential of Ti^+ is so much greater than the reported appearance potential (first ionization potential), it was concluded that Ti^+ is a result of fragmentation. Because of agreement between appearance potentials determined in this study with reported values for TiO^+ and TiO_2^+ and because of smooth ionization efficiency curves, the TiO^+ and TiO_2^+ are believed to originate from ionization of $\text{TiO}(\text{g})$ and $\text{TiO}_2(\text{g})$, respectively.

With the Knudsen cell at 2010°K and using 50 eV ionizing electrons, I^+ values were determined. They yielded $\text{TiO}^+ : \text{TiO}_2^+ : \text{Ti}^+ = 1.0 : 0.1 : 0.2$. Using the ratio of ionization cross sections for $\text{TiO}(\text{g})$ and $\text{TiO}_2(\text{g})$ reported by Hampson and Gilles⁷ and multiplier gains given by the inverse $\sqrt{M_1}$ proportionality, it was concluded that $P_{\text{TiO}} : P_{\text{TiO}_2} = 1.0 : 0.2$. Thus, reaction (3) is the predominant vaporization reaction.

The Ti_2O_3 - Ti_3O_5 solid mixture was placed in a W Knudsen effusion cell with an orifice with an effective area of 0.01445 cm^2 . To measure the rate of mass loss from the effusion cell while at high temperature, the

Table VIII. Appearance Potentials

Species	Appearance Pot., eV (this study)	Appearance Pot., eV (reported)
Ti^+	14.5	6.82 ^a
TiO^+	7.2	6.2 - 7.9 ⁷
TiO_2^+	12.0	10.3 ⁷

(a) C. E. Moore, "Ionization Potentials and Ionization Limits
Derived from the Analyses of Optical Spectra," NSRDS-NBS
34 (1970).

Knudsen cell was hung from a vacuum balance which had been described previously by Suzuki and Wahlbeck.¹⁰ From the rate of mass loss measurements, one may calculate the vapor pressure of TiO(g) assuming that $P_{\text{TiO}} : P_{\text{TiO}_2} = 1.0 : 0.2$.

Data for the vapor pressure of TiO(g) in equilibrium with $\text{Ti}_2\text{O}_3(\text{s})$ and $\text{Ti}_3\text{O}_5(\text{s})$ are given in Table IX. These data yield a $D^\circ[\text{TiO(g)}]$ value of $161.256 \pm 0.384 \text{ kcal mole}^{-1}$. Experiments are planned which would utilize an orifice of smaller size.

There is no obvious explanation as to why this value of $D^\circ[\text{TiO(g)}]$ is larger than the value reported by Drowart et al.⁵ Both values have uncertainties of ca. 3 kcal mole^{-1} based on scatter in the data and uncertainties in other thermodynamic properties which are required.

B. Gas-Surface Interactions

Gas-surface interactions play a vital role in many possible chemical studies. In earlier studies performed in this laboratory on the effusion of gases, it became clear that one of the most important interactions in the Knudsen cell was the gas-surface interaction. In addition, gas-surface interactions play an important role in catalysis and in the effects of gaseous species on space vehicles.

It was proposed that two experiments be performed. They are:

(1) determination of angular distributions of molecules reemitted from surfaces and (2) determination of mean residence times of species on surfaces. The following paragraphs will describe the current status of the work. No results have been obtained to date.

1. Spatial distribution experiment (B. C. Mikuska)

When molecules strike a surface, there are many possible events which may occur. They are: (1) reflection with poor thermal accommodation,

Table IX. Data for $\text{Ti}_2\text{O}_3(\text{s}) \rightleftharpoons \text{Ti}_3\text{O}_5(\text{s}) + \text{TiO}(\text{g})$

Run No.	True Temp °K	$P_{\text{TiO}(\text{g})}, \text{atm}$	ΔG_T° kcal	$T \left\{ \frac{G_T - H_{298}^\circ}{T} \right\}_{\text{TiO}} + \frac{G_T - H_{298}^\circ}{T}_{\text{Ti}_3\text{O}_5} - 2 \frac{G_T - H_{298}^\circ}{T}_{\text{Ti}_2\text{O}_3}$	ΔH_{298} kcal	$D^\circ(\text{TiO})$ kcal
2	2010	3.1848×10^{-7}	59.7469	(64.9719 + 85.9045 - 2 x 52.5585)	151.7233	161.343
3	2022	3.6856×10^{-7}	59.5166	(65.0162 + 86.1607 - 2 x 52.7319)	151.9485	161.116
4	1995	2.7056×10^{-7}	59.9471	(64.9158 + 85.5807 - 2 x 52.339)	151.355	161.710
5	2032	4.3096×10^{-7}	59.1795	(65.0531 + 86.3742 - 2 x 52.8764)	151.990	161.075
6	1977	1.6208×10^{-7}	61.4192	(64.8467 + 85.1834 - 2 x 52.069)	152.1479	160.917
7	2043	5.6656×10^{-7}	58.3894	(65.0937 + 86.6091 - 2 x 53.0353)	151.616	161.449
8	1968	1.3344×10^{-7}	61.9015	(64.8121 + 84.9848 - 2 x 51.934)	152.2896	160.775
9	1957	1.3328×10^{-7}	61.5585	(64.7699 + 84.7420 - 2 x 51.769)	151.5294	161.536
10	1947	0.8944×10^{-7}	62.7894	(64.7315 + 84.5213 - 2 x 51.6190)	152.3802	160.605
11	1985	2.4624×10^{-7}	60.0193	(64.8774 + 85.3600 - 2 x 52.1890)	151.0502	161.935
12	1936	0.8704×10^{-7}	62.5393	(64.6892 + 84.2785 - 2 x 51.454)	151.7109	<u>161.354</u>

Av. 161.256 ± 0.384

(2) lobular reflection with varying extents of thermal accommodation, (3) adsorption, (4) adsorption followed by reevaporation with usually good thermal accommodation, (5) surface migration, or (6) condensation. In the experiment which is being set up under this section, the distribution of molecules restituted to the gas phase from a well-defined surface will be determined. This will allow a study of the above effects under categories 1, 2, and 4.

In previous effusion studies in this laboratory, the effusion of CsCl vapor from Ni effusion cells has been studied. In the study which is being attempted here, the interaction of gaseous CsCl with a Ni surface will be examined initially.

The apparatus which has been designed is shown in Figure 1. A molecular beam is produced from an oven located at X which is heated to temperature T_1 (T_1 establishes the internal energy distribution). A velocity selector on the molecular beam selects molecules within a narrow velocity range to pass (the velocity selector established the translational energy). The molecular beam strikes the surface at S which is at temperature T_2 . The surface may be turned to allow variation in incidence angle. The surface will be well characterized and from a single crystal. Surface characterization will be performed by scanning electron microscopy. Clean surfaces will be prepared by evaporation of Ni onto the crystal surface. The molecules evaporating from the surface will be detected by D (initially a surface ionization detector). In initial experiments energy analysis of evaporating molecules will not be performed.

The apparatus will be mounted on the base plate of a large metal bell jar. The pumping system is Ultek Model TNB-C. The velocity selector will be the one previously used in the molecular effusion studies. Experience

Figure 1 - Schematic Representation of Gas-Surface
Interaction Apparatus

gained from the effusion studies would be of great value in working with the effusion sources and surface ionization detectors.

Construction of the apparatus is nearly finished. No data are available at this time.

2. Mean Residence Time Experiment (L. W. Huang)

Two factors are associated with surface migration. They are (1) mean residence time of molecules on the surface and (2) surface diffusion coefficient. In the experiment which will be discussed in this section, the design of an apparatus will be presented which will enable the measurement of mean residence times.

Because of previous interest in gaseous CsCl on Ni, the initial experiments will be performed with a pulsed molecular beam of CsCl on a well characterized Ni surface.

In Figure 2 is a schematic representation of an apparatus that has been designed to measure mean residence times of CsCl on Ni surfaces. The molecular beam of CsCl(g) originates at X, a double oven effusion cell with a conical orifice. The beam will be collimated by the slits indicated in Figure 2. The pulsing of the beam will be accomplished with a rotating chopper blade. The pulsed molecular beam will strike the surface S mounted at a 45° angle to the beam and protected by a cylindrical wall. Molecules evaporating from the surface will be sampled at 45° by a surface ionization detector. The time dependence of the signal from the detector will be studied.

The apparatus has been constructed and preliminary runs have shown that data can be acquired. The signal from the surface ionization detector (a current) has been allowed to flow through a 10^8 ohm resistor to ground. The voltage across the resistor has been amplified by a fast rise

Fig. 2.

time amplifier and then sent to a fast rise time oscilloscope, Tektronix, Model 543A.

Samples of output data are given in Figure 3. The experimental parameters associated with these data are given in Table X. These data are the first data recorded with this apparatus. Our immediate objective is to improve the data so that accurate residence times can be calculated. The data do indicate that results can be obtained.

(A)

(B)

(C)

 I^+

TIME

FIG.3

Table X. Experimental Parameters Associated with Figure 3

	Target	Front Oven	Back Oven	ordinate	abscissa
#20	666.5°K	920°K	905.5°K	0.1 mv/cm	20 ms/cm
#10	794°K	913°K	900°K	0.2 mv/cm	20 ms/cm
#15	867.5°K	918°K	904°K	0.2 mv/cm	20 ms/cm

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Appendix 1

Mass Spectrometric Observations of Gaseous Boron Selenides

by

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COO-1029-33

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Mass Spectrometric Observations of Gaseous Boron Selenides

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The vapor species evaporating from a sample prepared to be B_2Se_3 were identified with a time-of-flight mass spectrometer. The sample was heated to progressively higher temperatures over the range from ca. 100 to ca. 700°. The sample was contained in a tungsten Knudsen cell. Parent gaseous species believed to be present were $BSe_2(g)$ and $B_2Se_3(g)$. In addition there were products from the hydrolysis reaction with the condensed B_2Se_3 phase. These results are compared with those for the B-S system by Gilles, *et al.* The B-S and B-Se systems show similar vaporization behavior; the principal difference observed was the absence of gaseous polymers of BSe_2 and B_2Se_3 .

Introduction

Previous investigations of the B-Se system have been restricted to the condensed state. In two recent studies by Hutchinson and Eick¹ and Cueilleron and Hillel,²

$B_2Se_3(s)$ was prepared. Hutchinson and Eick¹ reported transformations at several temperatures, infrared spectra of $B_2Se_3(s)$, and values of X-ray diffraction interplanar spacings. Cueilleron and Hillel² reported different infrared and X-ray diffraction data; in addition they noted the reaction of B_2Se_3 and silica. The latter

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(2) J. Cueilleron and R. Hillel, *Bull. Soc. Chim. France*, **8**, 2073 (1967).

authors recommended a preparation procedure to avoid the reaction of B_2Se_3 and silica.

Recently Boryakova, *et al.*,³ reported a phase diagram study of the B-Se system with compositions principally from B_2Se_3 to Se. They reported that there is no compound formation between B_2Se_3 and Se; $BSe_2(s)$ was not found. The only compound that they found was $B_2Se_3(s)$ which melted at 480° . On both sides of B_2Se_3 , they reported that the compositions have liquidus temperatures below 480° .

Gaseous boron sulfides have been reported by Gilles, *et al.*⁴⁻⁸ Mass spectrometric investigations of gaseous products from the vaporization of $B_2S_3(s)$ (of variable composition) and the thermal decomposition of $HBS_2(s)$ revealed polymeric species of boron and sulfur with masses extending beyond 850. Because of the chemical similarities between sulfur and selenium, the boron-selenium system seemed likely to produce interesting gaseous species.

Experimental Section

Samples.—All samples of B_2Se_3 prepared for this study of the B-Se system were prepared from the elements. Boron of 99.15% purity was obtained from Matheson Coleman and Bell Co. Selenium had a stated purity of 99.999+ % with impurities being Te, Cu, As, and Si, each less than 0.0001%; the selenium was obtained from the American Smelting and Refining Co., South Plainfield, N. J.

Chemical reaction of the elements was accomplished by heating weighed portions of them in an evacuated ampoule. In initial preparations (method 1), the sample was heated at 490° for 24 hr in a quartz or Pyrex ampoule. In later preparations (method 2), a method suggested by Cueilleron and Hillel² was followed. The quartz ampoule was initially washed with 25% HF solution; the interior surface was then carbonized. In this method, the sample was heated at 750° for 4 hr. The carbonized interior surface prevented the attack of the sample on the quartz at elevated temperatures. In both methods, there is no reason to believe that the reaction was incomplete. No chemical analyses of samples were performed.

A portion of a sample prepared by method 2 was examined by X-ray powder diffraction. The absence of diffracted lines indicated that the sample was amorphous.

The samples of B_2Se_3 prepared in this study were very reactive with H_2O , either in liquid form, as moisture present in the atmosphere, or at low pressures in a drybox filled with argon, prepurified grade, 99.998% minimum purity, obtained from the Matheson Co. One of the products of the reaction between $B_2Se_3(s)$ and H_2O is $H_2Se(g)$; $H_2Se(g)$ can be prepared in large quantities by this reaction. Samples were placed in Knudsen cells in the drybox. Transfer of Knudsen cells to the mass spectrometer was done as quickly as possible so as to minimize contact with the atmosphere.

Mass Spectrometry.—The mass spectrometer used in this study was a time-of-flight mass spectrometer, Bendix Model 12-107. The circuits of Model 12-107 were modified following a suggestion by Studier;⁹ the resolution was improved so that it was at least 350 with a maximum detectable mass of ca. 5000 and

with a sensitivity such that pressures as low as 10^{-9} atm in the Knudsen cell could be measured. The inlet system to the mass spectrometer was a high-temperature Knudsen cell source following a design similar to that of Chupka and Inghram.¹⁰

The Knudsen cell in this study was fabricated from swaged tungsten rod. It was heated by radiation from a hot tungsten filament. Samples were heated in successive steps to higher temperatures with mass spectra taken at each step.

Temperatures of the Knudsen cell were ascertained by a calibration chart prepared by comparing power settings and chromel-alumel thermocouple readings. It is estimated that the uncertainties in temperature are within $\pm 10^\circ$.

Ionization of gaseous species in the mass spectrometer was accomplished by electron bombardment usually at 50 eV.

Mass scans were recorded with a strip chart recorder. Values of the mass:charge ratio for ions observed in a mass spectrum were determined by counting peaks (including background) from easily recognized species or by construction of a calibration chart of mass:charge *vs.* (chart position)². Isotopic distributions of species also proved valuable for identification of sets of peaks in the spectra.

Results

When the samples of B_2Se_3 , prepared by either of the two methods, were heated, gaseous atomic and molecular products were observed in the mass spectrometer. Identification of these species revealed two types of molecules (series 1 and 2). Series 1 has as its members species with B and Se: B^+ , selenium and its polymers— Se^+ , Se_2^+ , Se_3^+ , Se_4^+ , Se_5^+ , Se_6^+ , Se_7^+ — BSe_2^+ , $B_2Se_3^+$, and usually in small quantities BSe^+ , $B_2Se_2^+$, and BSe_3^+ ; there is weak evidence for $B_3Se_3^+$ and $B_2Se_4^+$. Series 2 has as its members species with B, Se, and H: H_2Se^+ , $H_2Se_2^+$, $H_2BSe_2^+$, and perhaps $H_2B_2Se_3^+$.

Species designated by X^+ and H_2X^+ will have the same intensity *vs.* mass distribution caused by the isotopic distributions of elements constituting X and the nearly monoisotopic nature of H; the intensity *vs.* mass distribution for H_2X^+ will be shifted 2 mass units higher than for X^+ . Through intensity *vs.* mass distributions, the presence of series 2 species was detected.

In addition to the above two series of species, the following peaks were observed: a set centering on mass 71, a set at 108 (Se isotopic distribution), and a set at 136 (Se isotopic distribution plus H_2Se). It is believed that these peaks are associated with species containing oxygen such as $HB_2O_3^+$ (71), $HBOSe^+$ (108), and $H_2B_2O_2Se^+$ (136). Oxygen was probably introduced into the samples by the hydrolysis reaction previously mentioned.

In Table I may be found data giving intensities of different species for a sequence of heatings on a single sample (prepared by method 1). During initial heating of a sample (not indicated in Table I), the principal gaseous species were Se and its polymers. At temperatures of ca. 300° , $BSe_2(g)$ was observed; see scans 2-4. Gaseous B_2Se_3 was observed only when the samples were heated to temperatures of ca. 500° ; see scans 12, 15, 16, and 19.

Table II contains data for heatings in which only series 1 species were observed; Table III is a similar

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TABLE I
INTENSITIES OF SPECIES IN A SEQUENTIAL VAPORIZATION^a

Scan	Temp, °C	¹¹ B	⁸⁰ Se	¹¹ BSe	¹⁰⁰ Se ₂	¹¹¹ BSe ₂	¹⁰⁰ Se ₃	¹¹ BSe ₃	¹¹¹ B ₂ Se ₃	¹⁰⁰ Se ₄	Se	Se ₂
2	285	u	>100 _H		3 _H	4 _H						
3	323	u	>100 _H		2 _H	16 _H						
4	362	u	95 _H		9	54 _H						
5	393	u	>100		37 _H	5 _H	4			4	1	9
7	425	u	55 _H		84	2	1			2		
12	567	u	>100		4	10 _H			3			
15 ^b	645	u	>100			31			17			
16	672	u	69 _H			24 _H			6			
19	...	u	>100		2 _H	20 _H			8			

^a Definitions: u, mass not scanned; H, both column species and column species + H_n present; no entry, intensity too small to observe. All data are from set II. ^b Probably no hydrogen.

TABLE II
SERIES 1 SPECIES AND THEIR INTENSITIES^a

Set	Scan	Temp, °C	¹¹ B	⁸⁰ Se	¹¹ BSe	¹⁰⁰ Se ₂	¹¹¹ BSe ₂	¹⁰⁰ B ₂ Se ₂	¹⁰⁰ Se ₃	¹¹ BSe ₃	¹¹¹ B ₂ Se ₃	Se ₄	Se ₅	Se ₆
II	7	425	u	55 _H		84	2		1			2		
II	15	645	u	>100			31				17			
I	1	...		>100		57	12		1		3	1		4
I	2	480	9	>>100		43	4		4		1	5		8
IV	3 ^b	592	2	>>100	21	>100	68	10		2	37			
IV	4	645	u	~100	75 _H	83	>100	23			74			

^a See footnote a of Table I for meanings of symbols. ^b High-mass species appeared.

TABLE III
SERIES 2 SPECIES AND THEIR INTENSITIES^a

Set	Scan	Temp, °C	¹¹ B	⁸⁰ Se	¹¹ BSe	¹⁰⁰ Se ₂	¹¹¹ BSe ₂	¹⁰⁰ B ₂ Se ₂	¹⁰⁰ Se ₃	¹¹ BSe ₃	¹¹¹ B ₂ Se ₃	Se ₄	Se ₅	Se ₆
II	2	285	u	>100 _H		3 _H	4 _H							
II	3	323	u	>100 _H		2 _H	16 _H							
II	5	393	u	>100 _H		37 _H	5 _H		4			4	1	9
II	7 ^b	425	u	55 _H		84	2		1			2		
II	12	567	u	>100 _H		4	10 _H				3			
II	16	672	u	69 _H			24 _H				6			
II	19	707	u	>100 _H		2 _H	20 _H				8			
III	3	663	u	u	u	5	15 _H				6			
III	5	693	u	>100		15	24 _H				9 _H	5		7

^a See footnote a of Table I for meanings of symbols. ^b Mostly nonhydrogen.

table for series 2. From these tables it can be noted that there were some cases in which series 2 species appeared and others in which they did not appear. The series 2 species which first appeared was H₂Se⁺; see Table II, set II, scan 7 in which it is the only series 2 species. Presumably the appearance of series 2 species depended upon the extent of the hydrolysis reaction discussed previously. The same trends with temperature as indicated for Table I may also be observed in these data although different series of heatings are combined.

Discussion

In the initial vaporization of samples of boron selenides, large ion intensities from selenium vapor and H₂Se(g) were observed. After Se had vaporized from the sample, B-Se ion species, series 1, and B-Se-H ion species, series 2, appeared in the mass spectrum.

Fragmentation of ions can occur in the electron bombardment ion source of a mass spectrometer. It is highly probable that the following ions occurred by loss of Se: BSe⁺, B₂Se₂⁺. The ion BSe₃⁺ (rarely observed) could occur by the loss of B from B₂Se₃. The

ion B⁺ was observed a few times; since B(g) could not occur under equilibrium conditions at these temperatures, it must have arisen from fragmentation. All of these suspected fragments were present in small quantities compared to their suspected parents.

The ions BSe₂⁺ and B₂Se₃⁺ are concluded to originate from the parent gaseous molecules BSe₂ and B₂Se₃. In early low-temperature heatings, BSe₂⁺ occurred either in the absence of B₂Se₃⁺ or when the intensity of B₂Se₃⁺ was much lower than the intensity of BSe₂⁺; i.e., the intensities of BSe₂⁺ and B₂Se₃⁺ are not related and in some mass spectra BSe₂⁺ was the highest mass species. Thus, BSe₂⁺ could be a fragment produced from B₂Se₃ but must be a parent species in some cases. The ion B₂Se₃⁺ has been observed frequently as the highest mass species. Since the pressure in the entire mass spectrometer was low (~5 × 10⁻⁷ mm) and the ion intensities of B-Se species were not appreciably higher than the background peak at mass 44 during the observation of BSe₂⁺ and B₂Se₃⁺, the origin of these species is not likely to be ion-molecule reactions.

The presence of species with masses greater than B₂Se₃ cannot be excluded. Indeed, data presented in Table II indicate that B₃Se₂⁺ and B₂Se₄⁺ may have

been present. It is possible that higher molecular weight species might have been present if higher temperatures had been achieved earlier in the vaporizations.

The presence of series 2 species probably arises from the reactivity of B_2Se_3 with $H_2O(g)$ even at low H_2O pressures. This hydrolysis reaction would be expected to introduce an oxygen contaminant also into the sample. The presence of oxygen in some species was deduced for sets of ions at masses 71, 108, and 136 as discussed previously. The presence of series 2 species $H_2BSe_2^+$ and $H_2B_2Se_3^+$ is assumed to be caused by parent species also bearing H atoms, probably $H_2-BSe_2(g)$ and $H_2B_2Se_3(g)$.

The data reported in Tables I-III indicate that the gaseous molecules BSe_2 and B_2Se_3 are thermally stable to 700° .

The results of this study of the boron selenides show some similarities to the studies of the vaporization of B_2S_3 ,^{4,5,8} the gaseous species observed were BS_2 , B_2S_3 , and their polymers. In the earlier studies,^{4,5} as the vaporization proceeded by heating to progressively higher temperatures, the higher molecular weight species decreased in importance leaving only $B_2S_3(g)$. In the study by Chen and Gilles,⁸ the gas composition was studied as a function of the composition of the condensed B-S phase. Congruent vaporization of B_2S_3 was found to produce only $B_2S_3(g)$ and its polymers. If the sample was S rich in comparison to B_2S_3 , $BS_2(g)$ and its polymers were found also. If the sample was S poor, then $B_2S_2(g)$ was detected in addition to BS_2^+ and $B_2S_3^+$. In the study of the thermal decomposition of HBS_2 ,^{6,7} it was concluded that HBS_2 initially lost large amounts of $H_2S(g)$, samples then lost gaseous polymers of HBX_2 , and finally the mass spectra of boron sulfides similar to those of the earlier studies were observed.

The appearance in this study of the vaporization of $B_2Se_3(s)$ of series 1 gaseous species may be compared

with what occurred with the similar vaporization of $B_2S_3(s)$ by Gilles, *et al.*^{4,5,8} The initial appearance of selenium and its polymers suggests that these B_2Se_3 samples were of high selenium activity. In later stages of the vaporization of these samples, the species $BSe_2(g)$ and $B_2Se_3(g)$ were observed. Gilles, *et al.*, in addition to $BS_2(g)$ and $B_2S_3(g)$, found gaseous polymers of BS_2 and B_2S_3 . If polymers of BSe_2 or B_2Se_3 were present, their importance was significantly less than in the case of the boron sulfides. The fact that vaporizations terminating at high temperatures led to B_2S_3 and BSe_2 (BSe_2^+ may be a fragmentation product at the end of the vaporization) and B_2Se_3 as the important gaseous molecular species shows the similarities in sulfur and selenium chemistry.

In the case of the boron selenides, the hygroscopic nature of the sample introduced H (and O) into the condensed phase. Initial stages of the vaporization showed large amounts of $H_2Se(g)$. In addition, $H_2-BSe_2(g)$ was observed. These results show similarities to the thermal decomposition of $HBS_2(s)$ studied by Gilles, *et al.*,^{6,7} in the case of HBS_2 , $H_2S(g)$ and $HBS_2(g)$ were observed. Further heating of the HBS_2 sample gave gaseous products as found in the vaporization of $B_2S_3(s)$. In this study of the B-Se system, further heating of samples showing H species, see Table III, gave rise to $B_2Se_3(g)$ just as vaporization of a sample showing only series 1 species.

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Appendix 2

Effusion VI. Velocity Distributions of Gaseous CsCl from
Near-Ideal and Right-Circular Cylindrical Orifices

by

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Effusion. VI. Velocity Distributions of Gaseous CsCl from Near-Ideal and Right-Circular Cylindrical Orifices*

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Velocity distributions have been measured for CsCl(g) effusing from double-oven effusion cells equipped with a near-ideal and nonideal right-circular cylindrical orifices. The back oven contained CsCl(s or l), and the front oven possessed an orifice. A multiple slotted-disk velocity selector was used to determine velocity distributions. The disks had slots cut at an angle (with respect to the selector axis) to provide improved transmission. Detectors utilized surface ionization. Data were acquired for states of CsCl(g) (as determined by temperatures of the back and front ovens) ranging from the molecular flow region into the transition region and for several effusion angles. The velocity distribution data may be summarized as follows: near-ideal orifice—data are in accord with the Maxwellian theoretical velocity distribution, and data show no dependence on Knudsen number (ratio of mean free path to orifice diameter) or effusion angle; nonideal cylindrical orifices—deviations from the Maxwellian distribution (with too many high-speed molecules or too few slow molecules) occurred at low pressures under molecular flow conditions, were largest at effusion angles near the axis of the orifice, and were enhanced by increasing pressure in the transition region. These data and previously published angular number distributions may be explained by introducing some specular reflection on the orifice wall for the nonideal orifices. Both sets of data were combined to yield angular momentum distributions.

INTRODUCTION

In previous papers in the series,¹⁻⁵ angular number distribution measurements have been reported for molecules effusing from a near-ideal orifice,¹ from right-circular cylindrical orifices,²⁻⁴ and from a conical orifice.⁵ These measurements were performed with pressures in the effusion cell such that the characteristics of flow were those of molecular flow with gas-phase collisions (to be distinguished from the cases in which pressure is so small that no gas-phase collisions occur within the effusion cell) and those of the transition region.

The following conclusions were reached in these studies:

(1) The cosine law of effusion is valid for the ideal orifice under conditions of molecular flow with gas-phase collisions.

(2) The Clausing⁶⁻⁹ theory for nonideal orifices (cylindrical and conical) has not been observed to be correct.

(3) A fluctuation phenomenon was observed for CsCl(g) effusing from Cu and Ni cylindrical orifices^{3,4} and a Cu conical orifice⁵ (the probability of effusion in the forward direction varied from run to run in the molecular flow region, whereas theory indicates that it should be constant).

(4) Fluctuations were found to be dependent on ΔT , the difference in temperature between the front and back ovens of a double-oven effusion cell.⁴

(5) An upper pressure limit was found for the molecular flow region separating it from the transition region.^{1,4}

(6) With increasing pressure in the transition region, the probability of effusion in the forward direction increases with the ideal orifice¹ and decreases with a long nonideal orifice.^{2-5,10}

In order to understand more fully the experimental data obtained in the previous experiments, velocity distributions of effusing molecules were measured in the study being reported here. Theoretically Maxwell¹¹ concluded that the velocity distribution of molecules in a gas should be

$$dN_C = AC^2 \exp(-mC^2/2kT) dC, \quad (1)$$

where dN_C is the number of molecules of mass m with speeds between C and $C+dC$ at temperature T . For molecules effusing from an orifice, the distribution as given by Eq. (1) must be multiplied by C . Velocity selectors are designed to operate at constant resolution, $R = \delta C/2C$. Thus, the distribution that exists from a velocity selector has the same form as given by Eq. (1) but must be multiplied by C^2 . For the "beam" molecules exiting from a velocity selector, the most probable velocity, C_{MP} , is

$$C_{MP} = (4kT/m)^{1/2} \quad (2)$$

and the average velocity, $\bar{C}$, is

$$\bar{C} = \frac{4}{3}(8kT/\pi m)^{1/2}. \quad (3)$$

Velocity distributions have been measured previously.^{12-22a} These measurements have demonstrated that the Maxwellian velocity distribution can be obtained if molecules effuse through near-ideal orifices from gases at very low pressures. Non-Maxwellian velocity distributions, caused by nonideal orifices and high gas pressures (transition region), have been noted.¹⁹⁻²² At high pressures a deficiency of slow molecules, in comparison with a Maxwellian velocity distribution, has been related to collisions occurring in the effusing beam by Esterman *et al.*¹⁷ and by Scott *et al.*²¹

In this study velocity distributions of molecules effusing from a near-ideal orifice and right-circular cylindrical orifices have been measured. These distributions

Fig. 1. Schematic representation of experimental apparatus. The apparatus consisted of two evacuated chambers separated by a bulkhead. The vacuum pumping system was described previously.¹ The effusion cell was located in Chamber 1 and the velocity selector in Chamber 2. Each disk of the velocity selector has 544 slits, 0.0424 cm wide. The entrance disk had a thickness of 0.1626 cm; all others were 0.8813 cm thick. The over-all length of the selector was 11.20 cm. The "helix" angle ϕ was 0.1666 rad.

have been measured as a function of the state of the gas behind the orifice and as a function of the effusion angle. The effusing gas was CsCl and was detected with a surface ionization detector.

The velocity distributions were measured by using a mechanical velocity selector. A velocity selector transmits molecules within a limited range of translational energies. The principle of operation of mechanical velocity selectors may be understood by considering the velocity selector of Miller and Kusch²⁰; it consisted of a solid drum with helical slots milled in its surface. With the drum rotating at a given rotational velocity, molecules which have entered a helical slot, which are moving parallel to the drum axis, and which have trajectories in accord with the rotational movement of

the helical slots (these molecules do not strike the slot walls) must have velocities within a narrow velocity range. The velocity of transmitted molecules with trajectories parallel to the helix, C , is given by

$$C/\omega = L/\phi \quad (4)$$

or

$$C = (L/\phi)\omega, \quad (5)$$

where L is the length of the velocity selector, ϕ is the angle through which the helical slot turns between entrance and exit positions, and ω is the rotational velocity of the velocity selector. Thus, C is proportional to ω .

Hostettler and Bernstein²³ constructed a velocity selector consisting of several thin disks with straight slots

TABLE I. Characteristics of the orifices.

Property	Near ideal	Short	Long
Material	Ni body with orifice in Pt	Cu OFHC	Ni grade A
<i>L</i> , length (mm)	0.013	0.196	0.440
<i>d</i> , diameter (mm)	0.50	0.42	0.34
<i>L/d</i>	0.026	0.466	1.294

radially cut into the disks. The velocity selector may be viewed as approximating sections of the Miller and Kusch²⁰ velocity selector. Trujillo *et al.*²⁴ have constructed a similar velocity selector.

A better approximation to the helical slot velocity selector of Miller and Kusch²⁰ would be achieved if the slots were milled in the disks at the helix angle rather than perpendicular to the disk as was suggested by Scott *et al.*²¹ The transmission to resolution ratio is larger in the case of the slanted slots.

The velocity distribution data gave valuable information about the trajectories of the molecules effusing from nonideal orifices. In addition the velocity distribution data and the angular number distributions already reported¹⁻⁴ yielded angular momentum distributions; the angular momentum distributions are of interest to those using the torsion effusion method and other momentum methods.²⁵

EXPERIMENTAL

Apparatus

The apparatus, which consisted of a rotatable effusion cell, a velocity selector, and surface ionization detectors, is represented schematically in Fig. 1.

The portion of the apparatus concerned with the rotation of the effusion cell has been discussed previously.¹ The effusion cell could be turned by means of the outside rotor. The axis of rotation of the effusion cell passed through the front plane and through the center of the orifice. The angular position θ was read from the exterior dial table.

The effusion cells were of the double-oven design as discussed previously¹; limited independence of temperature and of pressure of the effusing gas was permitted. The effusion cells were the same three utilized in studies of angular number distributions reported previously. The orifices of these effusion cells were a near-ideal orifice¹ and two right-circular cylindrical orifices.⁴ The geometries and construction materials for these orifices are given in Table I.

In all experiments, the back oven of the effusion cell was filled with "Specpure" quality CsCl(s) obtained from Johnson, Matthey, and Co. Reasons for the selection of CsCl have been given previously.¹

The design and principles of operation of the surface ionization detectors have been discussed previously.¹ A Re filament was used in these experiments. The detector indicated in Fig. 1 as being nearest the effusion cell (right) was used for the angular number distribution studies previously reported. The detector farthest from the effusion cell (left) was used to measure velocity distributions. The solid angle subtended by the farthest detector from the effusion cell orifice was 1.549×10^{-6} sr. The signal from the ion collector (see Fig. 1) was amplified with a vibrating reed electrometer; the conversion of ion currents to molecular intensities has been discussed previously.¹

The velocity selector used in this study was of the multiple disk type with slanted slots. Dimensions and quantities pertinent to the velocity selector are reported in Fig. 1.

The synchronous motor and variable frequency power supply used to drive the velocity selector were the same as used by Hostettler and Bernstein.²³

The rotational velocity of the velocity selector was indicated by a Hewlett-Packard tachometer indicator, Model 500C, using the signal from a magnetic pickup counting the number of teeth of an iron gear on the rotor shaft.

Procedure

Evacuation and effusion cell heating procedures have been discussed previously.¹

In order to achieve velocity distributions, the velocity selector was accelerated initially to the maximum rotational velocity which corresponds to a molecular velocity of 10.169×10^4 cm/sec. The velocity selector was allowed to decelerate with no power to produce a velocity distribution. For the near-ideal orifice and "long" orifice measurements, the tachometer and vibrating reed electrometer signals were fed to an X-Y

FIG. 2. Laboratory velocity distribution data. The ordinate is relative I^+ (signal from vibrating reed electrometer). The abscissa is velocity (C , signal from angular velocity tachometer); 1 cm = 3389.7 cm/sec. The signal-to-noise ratio of these data are of intermediate quality.

recorder during the deceleration of the velocity selector. For earlier measurements with both nonideal orifices, these two signals were simultaneously recorded with a two-pen recorder. An example of an experimental distribution is given in Fig. 2.

Velocity distributions were measured at several angular positions for several conditions of temperature and pressure of CsCl(g) .

RESULTS

General Comments

During analysis of the velocity selector data, visual observations of the velocity selector indicated that there were two paths through the teeth of the velocity selector; consequently, the velocity selector permitted molecules in two velocity ranges to pass through the selector. These two paths corresponded to $\phi_1 = 0.1666$ rad and $\phi_2 = 0.2443$ rad. Thus by Eq. (5), the two transmitted velocities were such that C_2/C_1 was 0.6818₂ (designated by F). In order to calculate the true velocity distribution from the experimental data, the relative transmissions of the velocity selector for these two velocities must be determined. From visual observations, the transmission of the second velocity was judged to be a little smaller than the first velocity. The relative transmission of the second velocity to the first was determined from near-ideal orifice velocity distributions by the following method.

In the Introduction, it was noted that previous studies of velocity distributions¹⁴⁻²² have shown that the velocities of molecules effusing from a low-pressure gas through an ideal orifice should be Maxwellian; particularly good evidence was seen in the works of Estermann *et al.*,¹⁷ Miller and Kusch,²⁰ and Scott *et al.*²² On this basis and on the basis of the agreement of angular number distributions from this near-ideal orifice¹ with the "cosine law of effusion," the velocity distributions were expected to be Maxwellian.

FIG. 3. Fitting of two Maxwellian velocity distributions to laboratory data. Data marked $\circ$ are from Run P13 (near-ideal orifice), $\theta = 0$. Maxwellian distribution for C_1 , ---; for C_2 , - - -; sum of two distributions, —. The agreement between data and sum curves is of intermediate quality. Abscissa, 1 unit $C_1 = 3389.7$ cm/sec. The difference between experimental and summation curves at large velocities is caused by experimental error.

FIG. 4. Comparison of calculated velocity distribution and Maxwellian distribution. Data: $\square$ and --- are from Run P13 (near-ideal orifice), $\theta = 0$; see Fig. 3. Maxwellian distribution is represented by $\circ$ and —. The agreement of these data with Maxwellian is of intermediate quality. Abscissa: 1 unit $C = 3389.7$ cm/sec.

The laboratory data for the near-ideal orifice were fitted to the sum of two Maxwellian distributions in which A_T , the relative transmission of the second velocity band to the first, was an adjustable parameter:

$$I = A[C^4 \exp(-mC^2/2kT) + A_T(FC)^4 \exp(-m(FC)^2/2kT)], \quad (6)$$

where the symbols have the same meanings as for Eq. (1). The fitting was accomplished by means of a non-linear least-squares program written by Struble.²⁶ An example of this fitting is shown in Fig. 3.

There are two sets of data taken by the two authors designated by run numbers with either K or P prefixes. The detector (left) positions were slightly different in these two series giving rise to two values of A_T .²⁷ For each series with the near-ideal orifice, the values of A_T were averaged (high-pressure runs with $K < 0.5$ were excluded). For the K series, $A_T = 0.4804 \pm 0.0943$ (average absolute deviation); for the P series, $A_T = 0.7082 \pm 0.0781$.

With the values of F and A_T known, the velocity distributions were calculated from the laboratory data for all runs.

The velocity distributions have been treated in three ways: (1) The entire velocity distribution was analysed, (2) the most probable velocity was determined, and (3) the average velocity was calculated. The velocity distributions (the aforementioned three items) have been examined for (1) agreement with the Maxwellian distribution, C_{MP}^{theor} , and $\bar{C}^{\text{theor}}$, (2) dependence on effusion angle θ , and (3) dependence on the state of

TABLE II. Conditions of CsCl(g); near-ideal orifice runs.

Run	$T(F)$ (°K)	$T(B)$ (°K)	ΔT	$Z \times 10^{-18}$ ^a (molecules $\text{cm}^{-2} \cdot \text{sec}^{-1}$)	P (mm Hg) ^b	K ^c	$\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor d}}$	$C_{\text{MP exptl}}/C_{\text{MP theor d}}$
K502	851	785	66	0.16	0.0017	46.24	1.0255	1.0366
K365	863	801	62	0.29	0.0031	26.14	0.9871	1.0046
K503	898	811	87	0.40	0.0044	19.11	0.9930	0.9928
K326	838	811	27	0.42	0.0044	17.83	0.9953	0.9989
K349	901	815	86	0.46	0.0051	16.68	0.9880	1.0147
P017	855	828	27	0.74	0.0080	10.17	0.9675	1.0332
K504	920	827	93	0.90	0.0101	8.62	0.9951	0.9772
K338	866	834	32	0.89	0.0097	8.44	1.0135	1.0189
K505	923	841	82	1.36	0.0153	5.72	0.9980	0.9730
K325	916	900	16	6.73	0.0753	1.15	0.9899	0.9767
P013	915	898	17	6.40	0.0716	1.21	0.9847	1.0412
P016	925	908	17	8.17	0.0918	0.95	0.9920	0.9837
P015	948	930	18	13.69	0.1557	0.58	1.0295	0.9712
P018	988	954	34	23.16	0.2689	0.35	0.9870	0.9772

^a $Z = p(2\pi mkT(F))^{-1/2}$.^b For $T(B) < 915^\circ\text{K}$, $\log_{10}p(\text{mm Hg}) = -[9960/T(B)] + 9.942$.
For $T(B) > 915^\circ\text{K}$, $\log_{10}p(\text{mm Hg}) = -[10210/T(B)] + 20.62 - 3.52 \log_{10}T(B)$.^c $K = \lambda_{\text{Maxwell}}/d$, $\lambda_{\text{Maxwell}} = kT/\sqrt{2}\pi\sigma^2p$, where $\sigma = 7.015 \text{ \AA}$ from the average of atomic and ionic diameters taken from N. A. Lange, *Handbook of Chemistry* (Handbook Publishers, New York, 1961), 10th ed.^d Data for $\theta = 0^\circ$.

TABLE III. Velocity distribution data for the three orifices.

Orifice	L/d	Runs	$\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor a}}$	$C_{\text{MP exptl}}/C_{\text{MP theor a}}$
Near-ideal	0.02	All	0.9961 ± 0.0046	0.9999 ± 0.0026
Short	0.466	$K > 1$	1.0117 ± 0.0170	0.9899 ± 0.0196
		$K < 1$	1.0941 ± 0.0209	1.0886 ± 0.0250
Long	1.294	$K > 1$	1.0338 ± 0.0053	1.0667 ± 0.0080
		$K < 1$	1.1011 ± 0.0095	1.1438 ± 0.0155

^a Averages of these quantities determined from entries in Tables II, III, and IV with standard deviations.

TABLE IV. Conditions of CsCl(g); short-orifice runs.

Run	$T(F)$ (°K)	$T(B)$ (°K)	ΔT	$Z \times 10^{-18}$ ^a (molecules $\text{cm}^{-2} \cdot \text{sec}^{-1}$)	P (mm Hg) ^b	K ^c	$\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor d}}$	$C_{\text{MP exptl}}/C_{\text{MP theor d}}$
K46	840	806	34	0.35	0.0037	26.36	1.0157	0.9731
K45	886	825	61	0.65	0.0072	13.88	0.9948	0.9864
K41	896	827	69	0.69	0.0077	13.12	1.0093	0.9661
K42	915	864	51	2.62	0.0293	3.53	0.9978	0.9722
K36	920	873	47	3.33	0.0373	2.78	0.9089	0.9035
K20	978	883	95	4.21	0.0487	2.26	1.0924	1.1127
K12	903	895	8	5.71	0.0634	1.60	1.0302	0.9849
K43	941	900	41	6.64	0.0753	1.41	1.0303	1.0198
K47	956	910	46	8.45	0.0965	1.12	1.0258	0.9907
K48	953	930	23	14.07	0.1558	0.69	1.0865	1.0846
K13	941	931	10	14.07	0.1594	0.67	1.0604	1.0554
K14	983	954	29	23.26	0.2690	0.41	1.1353	1.1259

^a See Footnote a of Table II.^b See Footnote b of Table II.^c See Footnote c of Table II.^d See Footnote d of Table II.

FIG. 5. Near-ideal orifice data. Upper plot: $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ vs $\log Z$; lower plot: ΔT vs $\log Z$. These values of $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ do not show any dependence on $\log Z$ or on ΔT .

CsCl(g) [pressure of CsCl(g), P_{CsCl} , and temperature of the front oven, $T(F)$].

Near-Ideal Orifice

In Table II may be found information pertaining to the runs performed with the near-ideal orifice. This information includes the state of CsCl(g) in the effusion cell and the quantities $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ and $C_{\text{MP}}^{\text{exptl}}/C_{\text{MP}}^{\text{theor}}$ derived from the velocity distribution data at $\theta=0$. The average of $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ values and of $C_{\text{MP}}^{\text{exptl}}/C_{\text{MP}}^{\text{theor}}$ values are indicated in Table III. Both of these values utilized all data regardless of P_{CsCl} and show good agreement with Maxwellian values of unity.

In Fig. 4 the experimental velocity distribution for a typical run is compared with the theoretical Maxwellian distribution. The agreement is seen to be good and is judged to be generally within the experimental error. The more notable deviations from the Maxwellian distribution are on the slow-velocity side of C_{MP} . This

FIG. 6. Near-ideal orifice data. $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ vs θ for runs under varying conditions.

Symbol	Run	K	ΔT
◇—	P17	10.2	27
△—	K505	5.71	82
□---	P13	1.21	17
○---	K325	1.15	16
○----	P16	0.953	17
▽...	P15	0.577	18
□....	P18	0.348	34

Within experimental error, there is no dependence of $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ on θ .

FIG. 7. Velocity distributions for the near-ideal orifice and long orifice I_{rel} vs C_{red} ($C_{\text{red}} = C/C_{\text{MP}}^{\text{theor}}$). Near-ideal orifice, —, Run K505, $\theta=0$, $K=5.72$; long orifice, ---, Run K77, $\theta=0$, $K=5.15$. The long-orifice data show a deviation from the near-ideal orifice data which agree with Maxwellian distribution.

agreement cannot be considered as an independent verification of the Maxwellian velocity distribution because of the manner in which the relative transmission of the two velocities was established as described earlier. However, there is no reason to believe that these distributions are not in accord with the Maxwellian distribution.

In Fig. 5 the effect of the pressure of CsCl(g) on the velocity distribution is examined; $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ at $\theta=0$ is plotted vs $\log Z$, where Z is the number of wall collisions in centimeters²·second⁻¹. From these data, increasing P_{CsCl} had no effect on the velocity distribution. In addition ΔT , $T(F)-T(B)$, for each run is indicated; this shows that $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ is not dependent on ΔT .

FIG. 8. Long-orifice velocity distribution data. Coordinates are $\bar{C}_R$ ($\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$), Z , and θ . The black balls are calculated points from the fitting of experimental data to Eq. (7). The smaller, gray points are experimental data. The view of the figure is taken at the angle of the "plane" of the calculated points. The enhancement of the deviation, as measured by $\bar{C}_R$, with pressure (or Z) and the dependence of $\bar{C}_R$ upon θ are seen by the position of the data "plane." θ axis, origin at $\theta=0$, 1 unit is 5° ; $\bar{C}_R$ axis, origin at $\bar{C}_R=0.95$, 1 unit is 0.04; Z axis, origin at $Z=0$, 1 unit is 2.5×10^{10} mol/sec.

TABLE V. Conditions of CsCl(g); long-orifice runs.

Run	$T(F)$ (°K)	$T(B)$ (°K)	ΔT	$Z \times 10^{-18}$ ^a (molecules cm ⁻² ·sec ⁻¹)	P (mm Hg) ^b	K ^c	$\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ ^d	$C_{\text{MP}}^{\text{exptl}}/C_{\text{MP}}^{\text{theor}}$ ^d
K76	887	855	32	1.74	0.0191	5.23	0.9917	1.0233
K77	900	856	44	1.78	0.0197	5.15	1.0384	1.0189
K78	926	854	72	1.97	0.0222	4.71	1.0360	1.1234
P35	914	868	46	2.56	0.0286	4.46	1.0261	1.0486
K55	865	860	5	2.06	0.0223	4.37	1.0506	0.9516
K82	881	876	5	3.32	0.0364	2.73	0.9956	1.0634
K83	895	882	13	3.93	0.0435	2.32	1.0127	1.0537
K81	948	881	67	4.06	0.0462	2.31	1.0239	1.0358
K80	938	881	57	4.08	0.0462	2.29	1.0347	1.0657
K79	925	882	43	4.22	0.0474	2.20	1.0380	1.0326
P32	936	894	42	5.72	0.0647	2.02	0.9774	1.0504
P25	935	894	41	5.72	0.0647	2.01	0.9766	1.0594
P28	1004	906	98	7.47	0.0874	1.60	1.0608	1.1159
P24	953	904	49	7.29	0.0832	1.59	1.0208	1.0848
K87	984	898	86	6.18	0.0716	1.55	1.0594	1.1220
K64	947	897	50	6.14	0.0698	1.53	1.0595	1.0859
K86	956	898	58	6.27	0.0716	1.51	1.0254	1.0653
K85	937	898	39	6.33	0.0716	1.48	1.0266	1.0167
K84	917	898	19	6.40	0.0716	1.44	1.0219	1.0600
P29	959	909	50	8.23	0.0941	1.42	1.0435	1.0756
K61	969	904	65	7.23	0.0832	1.31	1.0709	1.1129
K60	925	903	22	7.22	0.0811	1.28	1.0752	1.1149
P27	979	914	65	9.20	0.1064	1.28	1.0613	1.1083
P26	967	918	49	10.20	0.1172	1.15	1.0535	1.0961
K56	921	910	11	8.60	0.0965	1.08	1.0507	1.0815
P31	955	923	32	11.58	0.1320	1.01	1.0422	1.0682
K90	968	915	53	9.48	0.1090	1.00	1.0853	1.0857
K88	931	915	16	9.67	0.1090	0.96	1.0665	1.0870
K89	947	916	31	9.82	0.1116	0.96	1.0870	1.1621
K57	940	918	22	10.34	0.1172	0.90	1.1136	1.1517
P30	985	941	44	17.32	0.2008	0.68	1.0397	1.0715
K58	946	935	11	15.40	0.1750	0.61	1.1344	1.1651
P33	1007	955	52	23.46	0.2750	0.51	1.0864	1.1494
P34	1023	959	64	25.41	0.3003	0.47	1.0877	1.1390
K92	998	960	38	26.30	0.3069	0.37	1.1452	1.2316
K93	1021	961	60	26.57	0.3137	0.37	1.1482	1.2031
K91	985	960	25	26.47	0.3069	0.36	1.1176	1.1358

^a See Footnote a of Table II.^b See Footnote b of Table II.^c See Footnote c of Table II.^d See Footnote d of Table II.

In Fig. 6 the angular dependence of $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ is examined. No θ dependence is observed with the near-ideal orifice data under all pressure conditions examined in this research.

Cylindrical Orifices

In Tables IV and V may be found data for the short- and long-orifice experiments, respectively. In these tables, variables describing the state of CsCl(g) and values of $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ and $C_{\text{MP}}^{\text{exptl}}/C_{\text{MP}}^{\text{theor}}$ derived from the velocity distribution data are reported.

The dependence of the velocity distributions upon orifice length may be observed through the following

data. In Fig. 7 are given velocity distributions determined at $\theta=0$ under similar low-pressure conditions of CsCl(g) for the near-ideal and for the long orifices. The long-orifice data show deviations from the near-ideal orifice data. This same effect may be illustrated by means of the $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ and $C_{\text{MP}}^{\text{exptl}}/C_{\text{MP}}^{\text{theor}}$ data for θ of 0° or 15° ; see values of averaged quantities for $K>1$ in Table III. As L/d increases, the velocity distributions for cases where $K>1$ show deviations such such that $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ and $C_{\text{MP}}^{\text{exptl}}/C_{\text{MP}}^{\text{theor}}$ increase. The uncertainty is largest for the short-orifice data because this set of data is limited and was the first set determined.

The dependence of the velocity distributions for the short and long orifices on the parameters P_{CsCl} , θ , and ΔT was examined by fitting all data to the following equation:

$$\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}} = (A + BP_{\text{CsCl}} + CP_{\text{CsCl}}^2)(1 + D\Delta T)(1 + E\theta), \quad (7)$$

where A , B , C , D , and E are fitted parameters obtained from the nonlinear least-squares program.²⁶ Table VI summarizes the values of the parameters determined for each cylindrical orifice.

A graphical representation of the fitting of the experimental data by Eq. (7) may be seen for the long orifice in Fig. 8 and for the short orifice in Fig. 9. These two figures show that $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ increases with P_{CsCl} (or Z) and decreases with θ for both long and short orifices. The dependence of $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ and $C_{\text{MP}}^{\text{exptl}}/C_{\text{MP}}^{\text{theor}}$ upon P_{CsCl} may be noted also by comparison of averaged values of these quantities for $K > 1$ (low pressure) and for $K < 1$ (high pressure) given in Table III. Even with the scatter in the experimental data, these dependences upon Z and θ are significant.

The dependence of $\bar{C}_{\text{exptl}}/\bar{C}_{\text{theor}}$ upon ΔT was believed to be significant during preliminary analysis of the data. The analyses of the data using Eq. (7) lead to the temperature dependence as shown by the values of D reported in Table VI. For the long orifice the dependence on ΔT is small if not insignificant in comparison to the scatter in the data. For the short orifice, there is not very much data available for a reliable determination of the importance of a ΔT effect.

DISCUSSION

Near-Ideal Orifice

The velocity distributions for CsCl(g) effusing from a near-ideal orifice were found to agree with the theoretical Maxwellian distribution; see Figs. 4–6 and Tables II and III. The experimental velocity distributions, within experimental error, show no dependence on K , the Knudsen number (or Z or P_{CsCl}), on θ , the

FIG. 9. Short-orifice velocity distribution data. Photograph similar to Fig. 8; see caption of Fig. 8. The angle of this photograph was slightly below the "plane" of the black balls representing calculated $\bar{C}_R$. The light colored large balls represent calculated $\bar{C}_R$ values for two cases: The larger $\bar{C}_R$ corresponds to a very large ΔT case, and the smaller $\bar{C}_R$ corresponds to a very small ΔT case. θ axis, origin at $\theta = 0$, 1 unit is 5° ; $\bar{C}_R$ axis, origin at 0.95, 1 unit is 0.04; Z axis, origin at $Z = 0$, 1 unit is 2.5×10^{18} mole sec^{-1} .

effusion angle, or on ΔT , $T(F) - T(B)$. Effects due to collisions occurring within the effusing gas at small K were not observed in the K range used in these studies.

The near-ideal orifice gave experimental results which agreed excellently with theory. In earlier studies,¹ the angular number distributions for runs with $K > 8.16$ agreed with the cosine law of effusion. An assumption that has been made in developing the kinetic theory of gases for effusing molecules is that the molecules have a Maxwellian velocity distribution; these velocity distribution results are in accord with that assumption.

Nonideal Cylindrical Orifices

The experimental velocity distributions of molecules effusing from both the short and long nonideal cylindrical orifices showed deviations from the Maxwellian velocity distribution; this may be seen from data presented in Tables III–V and Figs. 7–9. These deviations occurred at low pressures under molecular flow conditions, were largest at effusion angles near the axis of the orifice, were enhanced by increasing pressure in the transition region, and perhaps increased with increasing ΔT (the experimental data have sufficient scatter so that the ΔT dependence is unknown).

These deviations from the theoretical Maxwellian velocity distribution were not likely to have been caused by apparatus difficulties. If deviations were caused by apparatus difficulties, they should have been observed with the near-ideal orifice case also.

Gas-phase collisions^{17,21} occurring during the effusion process can cause deviations from a Maxwellian theoretical velocity distribution. However, deviations seen at low pressures with the nonideal orifices could not be caused by the small number of such gas-phase collisions. The deviation's enhancement with pressure is believed to be caused by some other phenomenon than

TABLE VI. Values of parameters for Eq. (7).

	Long-orifice data		Short-orifice data	
	Value of parameter	Standard error	Value of parameter	Standard error
A	1.02113	0.01691	0.92736	0.02437
B	0.63290	0.23445	1.20296	0.29240
C	-0.59179	0.66074	-2.06507	0.97102
D	-0.00026	0.00019	0.00081	0.00032
E	-0.00155	0.00020	-0.00038	0.00021

increasing numbers of gas-phase collisions because there is no pressure dependence of velocity distribution for the near-ideal orifice experiments in the same high-pressure range.

The presence of $\text{Cs}_2\text{Cl}_2(\text{g})$, known to be present from thermodynamic data for $\text{Cs}_2\text{Cl}_2(\text{g})$ and observed to be present by Grimley and LaRue,²⁸ will not explain the deviations in velocity distribution since heavier mass species would cause an excess of slow molecules.

The deviations in velocity distributions for the non-ideal orifices could be caused by the presence of a vapor species of low mass also detectable by the surface ionization detector, e.g., $\text{Cs}(\text{g})$. Data from run P26 were analysed by fitting the data to an equation with two Maxwellian distributions, one for $\text{CsCl}(\text{g})$ and the other for $\text{Cs}(\text{g})$, with the ratio of $\text{Cs}(\text{g})$ to $\text{CsCl}(\text{g})$ being an adjustable parameter. The analysis of P26 showed that the deviation could be caused by a ratio of $\text{Cs}(\text{g})$ to $\text{CsCl}(\text{g})$ of 1.22. Thermal dissociation of CsCl producing $\text{Cs}(\text{g})$ could occur on the orifice wall. Molecular $\text{CsCl}(\text{g})$ is very stable; the equilibrium ratio of $P_{\text{Cs}}/P_{\text{CsCl}}$ is at the most 10^{-7} at 1000°K . The adsorbed population on the orifice wall decreases as one passes from the gas side of the orifice to the vacuum side. The adsorbed population of $\text{CsCl}(\text{g})$ would have to decrease by a factor of 10^{+10} in order to raise $P_{\text{Cs}}/P_{\text{CsCl}}$ to ~ 1 . Thus, the probability of $\text{Cs}(\text{g})$ leaving the orifice in significant amounts is very small.

Another possible source of low mass species is surface ionization which could have occurred on the Ni orifice wall. However, with so little thermal dissociation occurring, it is not probable that much $\text{Cs}^+(\text{g})$ could be produced by surface ionization of $\text{CsCl}(\text{g})$ on the orifice wall of the effusion cell.

If the orifice wall and nearby effusion-cell wall were at a temperature lower than $T(F)$ [the heater and thermocouple locations would not allow a temperature higher than $T(F)$], deviations would be introduced into the velocity distribution with an apparent excess of slow molecules. Because heat conduction to the orifice is better through thicker metal, the temperature of the orifice wall should be closest to $T(F)$ for the long orifice, the orifice case for which the deviation is largest. In addition, the observed deviations do not correspond to too many slow molecules. Thus, the deviation cannot be explained by a nonisothermal wall in the front oven.

With the removal of these possibilities of apparatus malfunction, gas-phase collisions, thermal dissociation, surface ionization, and nonisothermal conditions, it is concluded that the deviations observed were caused by effusing $\text{CsCl}(\text{g})$ molecules with a non-Maxwellian velocity distribution.

Because there is not absolute intensity data available, the observed deviations could arise from either too many fast molecules or too few slow ones. It is reasonable to believe that gas-phase collisions would

preferentially remove slow molecules; however, this effect does not appear to be significant by previous arguments.

In discussing the angular number distributions for $\text{CsCl}(\text{g})$ effusing from these same cylindrical orifices,⁴ the results of the present study were utilized. The conclusion was reached that both kinds of data could be explained only by introducing some specular reflection for the gas-orifice-wall interactions. These arguments lead one to believe that the deviations are due to too many fast molecules.

Specular reflection (or lobular reflection) has been experimentally observed in many cases, particularly cases of low-mass gas atoms impinging on surfaces consisting of heavy atoms. The surfaces usually have been degassed well and are of a single crystal. These results are generally in accord with the "cube" models of Stickney *et al.*^{29,30} Specular reflection has been observed with Ar and N_2 molecular beams impinging on polycrystalline Ni by Fisher, Hagena, and Wilmoth.³¹

If molecules are specularly reflected with increasing probability as the angle of incidence to the surface decreases and as the energy of the molecules increases, then the velocity distributions would be expected to be distorted with too many fast molecules effusing from the orifice in directions near the orifice axis, the experimentally observed θ dependence for the velocity distributions. The angular number distributions should then show too many molecules at small θ , and this is in accord with the experimental angular number distributions.⁴

Previously fluctuations in the probability of effusion in the forward direction were correlated with ΔT . This correlation was postulated to be connected with specular reflection. Thus, a correlation of the deviation from

FIG. 10. Angular momentum distribution data for the long orifice. $P_m(\theta) = P(\theta) \bar{C}/\bar{C}^{\text{theor}}$, where $P(\theta)$ is the probability density function derived from the angular number distribution data. —, $P(\theta)_{\text{Clausing}}(\bar{C}^{\text{theor}}/\bar{C}^{\text{theor}})$; theoretical Clausing angular number distribution with a Maxwellian velocity distribution. ---, $P(\theta)_{\text{exptl}}(\bar{C}^{\text{theor}}/\bar{C}^{\text{theor}})$; experimental angular number distribution, Run K69 (see Ref. 4), $\Lambda = 2.53$, with a Maxwellian velocity distribution. —·—, $P(\theta)_{\text{exptl}}(\bar{C}_{\text{exptl}}/\bar{C}^{\text{theor}})$; same experimental angular number distribution with a calculated $\bar{C}_{\text{exptl}}/\bar{C}^{\text{theor}}$ from Eq. (7). There is a larger momentum component in the forward direction than indicated by the theoretical distributions.

the Maxwellian velocity distribution with ΔT was expected. Unfortunately, the scatter in the experimental velocity distribution data was so large that no comments can be made regarding this variable.

Previously⁴ it was stated that when mean free path decreased (decreasing K) in the transition region, a larger fraction of the molecules entering the orifice undergo orifice-wall collisions. Thus if the pressure is increased, any wall effects would be enhanced. If specular reflection is occurring, more specular reflection should occur with more deviation in the velocity distributions. This would explain the pressure dependence observed in the velocity distribution data.

By combining angular number distributions and velocity distribution data as a function of θ , the angular momentum distribution may be calculated. See Fig. 10 for the angular momentum distribution for the long orifice. From the experimental angular momentum distribution, Searcy-Freeman factors for torsion effusion experiments may be calculated, i.e., ratio of the momentum component parallel to the orifice axis for the long orifice to the same quantity for the ideal orifice. With the experimental data for a low-pressure run, $P(\theta)_{\text{exptl}} \bar{C}_{\text{exptl}} / \bar{C}_{\text{theor}}$, and the orifice transmission probability, the Searcy-Freeman factor was 0.52; using $P(\theta)_{\text{Clausing}}$ (assuming a Maxwellian velocity distribution), the Searcy-Freeman factor was 0.50.³² The experimental Searcy-Freeman factor is 4% larger than the theoretical factor; this difference is significantly different from zero. This may be part of the explanation why torsion pressure measurements are consistently too large.

Conclusions

For the case of effusion from a near-ideal orifice, the Maxwellian velocity distribution describes the experimental results. When molecules effuse from a nonideal orifice (cylindrical orifices in this particular case), gas-surface interactions occur for those molecules which strike the orifice wall. Of presently known effects, the only known one which explains the results is the introduction of some specular (or lobular) reflection into the gas-surface interaction. This does not eliminate the possibility that some unknown phenomenon occurs.

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²⁶ G. Struble, "Non-linear Least Squares Curve Fitting Program," IBM 1620 General Program Library, 6.0.134.

²⁷ This conclusion has been justified through the analyses of data as a function of detector position.

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Appendix 3

Effusion. VII. The Failure of Isotropy of a Gas in an Effusion
Cell and the Transition Region

by

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Effusion VII. The Failure of Isotropy of a Gas in an
Effusion Cell and the Transition Region.

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Abstract.

A theory with a molecular model is presented for the transition region between the molecular flow region and the hydrodynamic flow region for the effusion of gases through orifices. The theory has as its basis a parameter which is associated with the failure of isotropy of the gas within the effusion container and which is calculated from the solid angle subtended by the vacuum opening of the orifice at the collision site of gaseous molecules within the effusion cell. This leads to modification of the kinetic theory equations for the ideal orifice for both the angular number distributions and the orifice transmission factors; these modified equations agree well with available experimental data. For orifices with orifice walls, the solid angle subtended by the orifice wall becomes an important parameter because the probability that a molecule has its trajectory such that it collides with the orifice wall depends upon that solid angle. A modification of the Clausing theory for non-ideal orifices appears to agree well with experimental angular distributions for the cylindrical orifice case. It should be possible to extend these calculations to other non-ideal orifice shapes.

I. INTRODUCTION

There have been a number of experimental studies with the purpose of understanding the basic processes involved in the effusion of gases through orifices. Of interest in this particular study is the transition region between molecular flow and hydrodynamic flow. Experimentally observed boundaries between the transition region and other regions are given in Table 1.

The effusion studies which have been performed are of two types: 1) angular number distribution determinations - the number of molecules effusing per second at angle θ with respect to the axis of the orifice through solid angle $d\omega$ and 2) orifice transmission factor determinations - the ratio of total number of molecules leaving the orifice per second to the total number of molecules per second leaving the ideal orifice (small opening in infinitesimally thin wall) as given by the kinetic theory of gases; i.e., $1/4 N\bar{C}A$, where N is the number of gaseous molecules cm^{-3} , $\bar{C}$ is the average velocity, and A is the orifice area. Experimental results are available for the near-ideal orifice; see Wang and Wahlbeck¹ for their results and for a summary of results from other investigators. In addition, experimental results

(1) K. C. Wang and P. G. Wahlbeck, J. Chem. Phys. 47, 4799 (1967).

are available for right-circular cylindrical orifices; see Wang and Wahlbeck². From these studies, the probability of

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effusion in the forward direction ($\theta = 0$) for the ideal orifice case increases with increasing pressure in the transition region, and the probability of effusion in the forward direction for the case of the long cylindrical orifice (length to diameter ratio of ~ 1.3) decreases with increasing pressure in the transition region.

Table I. Regions of Gas Flow.

Region

Molecular flow, gas-phase collisions not important see Ward <u>et al.</u> ^A	$\lambda > \text{I.D.}$, internal dimensions of effusion cell ^B $K > \text{I.D.}/d$; d , orifice diameter
Molecular flow, gas-phase collisions are important	$\text{I.D.} > \lambda > 8 d^1$ $\text{I.D.}/d > K > 8$
Transition region between molecular flow and hydrodynamic flow	$8 d > \lambda > \sim 0.01 d$ $8 > K > \sim 0.01$
Hydrodynamic flow	$0.01 d > \lambda$ $0.01 > K$

(A) J.W. Ward and M.V. Fraser, J. Chem. Phys. 50, 1877 (1969);
sixth member of a series.

(B) K , Knudsen number, is ratio of mean free path to orifice
diameter, λ/d .

Assumptions used in the kinetic theory of gases to derive the theoretical effusion equations are given in Table II. The assumption which is most likely to fail as one goes from the molecular flow region into the transition region is (4) the gas is isotropic at all points. The isotropy assumption is made so that geometrical parameters for the orifice are simple. In the transition region, the mean free path, λ , is very small and the last gas-phase collision that a molecule has is very near the orifice, a region of space where the gas certainly is not isotropic. Wu³ has realized that isotropic parameters are important

(3) Y. Wu, J. Chem. Phys. 52, 1494 (1970).

in studying thermal transpiration of a gas.

Narashima⁴ and Willis⁵ have presented a theory for the flow of gases.

(4) R. Narashima, J. Fluid Mech. 10, 65 (1961).

(5) D. R. Willis, J. Fluid Mech. 21, 21 (1965).

through orifices. They have used the solid angle subtended by the orifice at collision sites and have solved the flow equations. Their approach is different than that given in this paper; their results agree less well with experimental results than the equations presented in this paper.

The purpose of this article is to describe a modification of the kinetic theory of gases which will consider the transition region on the basis of the failure of the isotropy assumption.

II. ISOTROPY CONCEPT

The definition of the concept of isotropy may be made with the aid of Figure 1. The two elements of solid angle $\delta\omega_R$ and $\delta\omega_L$ are equal in size, both are centered on the same region of space, $\underline{Q}$, and are opposite in direction. The region of space at $\underline{Q}$ will be isotropic with respect to $\delta\omega$ if the same number of molecules have trajectories toward $\underline{Q}$ in both $\delta\omega_R$ and $\delta\omega_L$ and away from $\underline{Q}$ in both $\delta\omega_R$ and $\delta\omega_L$. The region of space at $\underline{Q}$ will be isotropic if the above is true for $\delta\omega$ pairs in all directions centered at $\underline{Q}$.

Consider molecules moving with trajectories aligned with the solid angles $\delta\omega_R$ and $\delta\omega_L$. Call this group of molecules the " $\delta\omega$ molecular group." The origin of molecules in the $\delta\omega$ molecular group may be from (S1) the collision in $\delta\omega$ of two molecules which need not be members of the $\delta\omega$ molecular group before collision and (S2) evaporation from a surface element in $\delta\omega$. Molecules

Table II. Assumptions Used in Kinetic Theory of Gases.

Ideal Orifice Case.

1. Molecules are identical masses with volumes which are insignificant in comparison with the total volume of the gas.
2. Interacting forces are absent between molecules.
3. Velocity distribution is Maxwellian.
4. Isotropy exists at all points in the gas.

Non-ideal Orifice Case.

In addition to the above four assumptions, the following assumption is made.

5. Cosine law of restitution
 - A. Reevaporation at point of impact, Clausing^{12,13} .
 - B. Reevaporation coupled with surface diffusion, Hirth, Ruth, and Winterbottom¹⁴⁻¹⁶ .

may be removed from the $\delta\omega$ molecular group through (R1) collision with a non-group member, (R2) collision with a group member, and (R3) condensation onto a surface element. These source and termination mechanisms are schematically represented in Figure 1.

Consider a $\delta\omega_R$ which has a surface element (wall of the gas container). Molecules moving away from $\underline{O}$ will be removed from the $\delta\omega$ molecular group by (R3). Molecules moving toward $\underline{O}$ may originate by (S2). With the molecules moving toward $\underline{O}$ from (S2), one will remove some molecules moving away from $\underline{O}$ by (R2) reducing the number of molecules in the $\delta\omega$ molecular group.

Consider now the removal of the surface element in $\delta\omega_R$ in order to produce the effusion orifice. For molecules moving away from $\underline{O}$ through $\delta\omega_R$, one loses termination (R3); i.e. these molecules pass through the orifice. In addition one loses a source of molecules going toward $\underline{O}$, (S2). Because there are fewer molecules moving toward $\underline{O}$, there are fewer terminations of the type (R2). Consequently, there is an increased probability that molecules will pass through $\delta\omega_R$ away from $\underline{O}$ and through the effusion orifice because of the fewer terminations of type (R2) caused by the fewer molecules in $\delta\omega_R$ moving toward $\underline{O}$, (S2). This increase in probability for molecules moving away from $\underline{O}$ and toward the opening in the wall (the effusion orifice) should be proportional to the size of the vacuum opening; appropriate parameters will be introduced into the effusion theory.

III. IDEAL ORIFICE

The cosine law for effusion of a gas through an ideal orifice may be derived in the following way. In Figure 2 an orifice is indicated and a cylinder of infinite length is drawn from the orifice into the gas container. One desires the number of molecules effusing at angles between θ and $\theta + d\theta$ or whose

trajectories are within the solid angle $d\omega$. These molecules must originate within the cylinder. Consider molecules which have ^a gas-phase collision in the cylinder at distances from the orifice between L and $L + dL$. The number of molecules which escape per second from this group, $dN_{\theta,L}$, will be

$$dN_{\theta,L} = (2 \times \text{Number of binary collisions cm}^{-3} \text{ sec}^{-1}) \times \\ (\text{Volume of cylinder element}) (\text{Probability that} \\ \text{molecules will have trajectories in } d\omega) \times \\ (\text{Probability of escape}). \quad (1)$$

Let Z_{11} be the number of binary collisions $\text{cm}^{-3} \text{ sec}^{-1}$. The volume element is $A \cos \theta dL$, where A is the cross-sectional area of the cylinder. The probability that molecules (considering a large number of molecules) have trajectories in $d\omega$ after collision is $d\omega/4\pi^+$; this is equivalent to saying molecules may leave a collision site, on the average, in any direction with

(+) It may be noted that $d\omega$ should be defined as the solid angle subtended by the detector from the collision site; $d\omega = ds/\rho^2$, where ds is the spherical element of area of the detector at a distance ρ from the collision site. The distance ρ equals $L + \rho_0$, where ρ_0 is the distance from the orifice to the detector. If $\rho_0 \gg L$, then $d\omega = ds/\rho_0^2$.

equal probability. The probability for escape can be found from the free path distribution; the number of molecules with paths between L and $L + dL$ is given by⁶

(6) E.H. Kennard, Kinetic Theory of Gases (McGraw-Hill Book Co., New York, 1938).

$$dN_L = 1/\lambda e^{-(L/\lambda)} dL. \quad (2)$$

The probability that the path will be greater than L is $e^{-(L/\lambda)}$. This will be the probability of escape only if the gas is isotropic. By substitution into equation (1)

$$dN_{\theta,L} = 2 Z_{11} A \cos \theta dL (d\omega/4\pi) e^{-(L/\lambda)}. \quad (3)$$

The number of molecules effusing at angle θ through solid angle $d\omega$ per second, dN_{θ} , may be found by integration over values of L from 0 to ∞ ;

$$dN = 2Z_{11} A \cos \theta (d\omega/4\pi) \int_0^{\infty} e^{-(L/\lambda)} dL, \quad (4)$$

$$dN_{\theta} = 2Z_{11} A \cos \theta (d\omega/4\pi) \lambda. \quad (5)$$

By the Maxwell theory for mean free paths, $\lambda = (\bar{N})/2Z_{11}$; thus, equation (5) becomes

$$dN_{\theta} = (\bar{N}/4\pi) A \cos \theta d\omega, \quad (6)$$

the usual form of the cosine law of effusion.

If the probability for escape is increased by the failure of isotropy caused by the presence of the orifice, then it should be larger than $e^{-(L/\lambda)}$. The number of molecules in the $\delta\omega$ molecular group moving toward $\underline{O}$ through $\delta\omega$ (defined by the orifice opening; $\delta\omega_R$ in Figure 1) will be decreased by an amount proportional to $\delta\omega$ (a quantity related to the size of the vacuum opening). The probability for effusion (for molecules moving through $\delta\omega$ away from $\underline{O}$) should be increased by a quantity proportional to $\delta\omega$. Therefore, assume that the probability of escape is given by

$$e^{-(L/\lambda)} [1 + E(\delta\omega(\theta)/2\pi)] \quad (7)$$

where $\delta\omega(\theta)$ is the solid angle subtended by the orifice at the collision site. The larger the orifice area, the larger will be $\delta\omega(\theta)$, and the larger will be the anisotropic character of the gas at the collision site.

Making the new substitution of expression (7) into equation (1), one obtains

$$dN_{\theta,L} = 2Z_{11} A \cos \theta dL (d\omega/4\pi) e^{-(L/\lambda)} [1 + B(\delta\omega(\theta)/2\pi)] \quad (8)$$

As before, dN_{θ} is found by integration over L from 0 to ∞ ;

$$dN_{\theta} = 2Z_{11} A \cos \theta (d\omega/4\pi) \lambda \left[\int_0^{\infty} e^{-(L/\lambda)} dL + B \int_0^{\infty} (\delta\omega(\theta)/2\pi) e^{-(L/\lambda)} dL \right], \quad (9)$$

or

$$dN_{\theta} = N\bar{C}A \cos \theta (d\omega/4\pi) \left[1 + (B/\lambda) \int_0^{\infty} (\delta\omega(\theta)/2\pi) e^{-(L/\lambda)} dL \right] \quad (10)$$

One must evaluate the integral in equation (10) to obtain a final equation. For the case of $\theta = 0$, see Figure 3. The solid angle of a cone with half-angle ψ may be calculated from

$$\delta\omega(0) = \int_0^{\psi} 2\pi \sin \phi d\phi = 2\pi (-\cos \phi) \Big|_0^{\psi} = 2\pi (1 - \cos \psi) \quad (11)$$

In the case represented by Figure 3, $\cos \psi = L/\sqrt{L^2 + r^2}$. Thus,

$$\frac{\delta\omega(0)}{2\pi} = 1 - L/\sqrt{L^2 + r^2}, \quad (12)$$

where r is the radius of the orifice. From Erdélyi⁷

(7) A. Erdélyi, Editor, Tables of Integral Transforms, Vol. 1 (McGraw-Hill Book Co., 1954), p. 136.

$$\begin{aligned} \delta\bar{\omega}(0)/2\pi &= 1/\lambda \int_0^{\infty} (1 - L/\sqrt{L^2 + r^2}) e^{-(L/\lambda)} dL \\ &= 1 - \pi r/2\lambda [H_1(r/\lambda) - Y_1(r/\lambda)] + r/\lambda \end{aligned} \quad (13)$$

where $H_1(x)$ is a Struve function and $Y_1(x)$ is a Bessel function of the second kind. To find $\delta\omega(\theta)$, the following assumption is made which is valid certainly for large L :

$$\delta\omega(\theta) = \cos \theta \delta\omega(0). \quad (14)$$

The modified cosine law may be written as

$$dN_{\theta} = N\bar{C} A \cos \theta (d\omega/4\pi) [1 + B \cos \theta (\delta\bar{\omega}(0)/2\pi)] \quad (15)$$

The constant B may be determined through integration to find the total number of effusing molecules. To perform that integration, $d\omega = 2\pi \sin \theta d\theta$, and integration is performed over θ from 0 to $\pi/2$;

$$\begin{aligned} N &= N\bar{C} A \frac{1}{2} \left[\int_0^{\pi/2} \cos \theta \sin \theta d\theta \right. \\ &\quad \left. + B \delta\bar{\omega}(0)/2\pi \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \right] \end{aligned} \quad (16)$$

or

$$N = 1/4 N\bar{C} A [1 + 2/3 B \delta\bar{\omega}(0)/2\pi]. \quad (17)$$

At the hydrodynamic flow limit, $N/(1/4 N\bar{C} A) = 1.65$ from the data of Carlson et al.⁸ and $\delta\bar{\omega}(0)/2\pi = 1$. Thus, $B \approx 1$ and

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- (8) K.D. Carlson, P.W. Gilles, and R.J. Thorn, J. Chem. Phys. 38, 2725 (1963).
-

is assumed to be unity.

It is possible to compare both of these equations; i.e., (15) for angular number distributions and (17) for orifice transmission factors, with experimental data. This is done in Figure 4 where $N/(1/4 NCA)$ is plotted against $\delta\bar{\omega}(0)/2\pi$ and in Figure 5 where $P(\theta)_{\text{exp}} N/(1/4 NCA)$ is plotted against $\delta\bar{\omega}(0)/2\pi$.

The $N/(1/4 NCA)$ data plotted in Figure 4 are taken from Carlson et al.⁸ who studied the effusion of Hg vapor and from a set of preliminary data from Wey and Wahlbeck⁹ who studied

- (9) S.-J. Wey and P.G. Wahlbeck, unpublished data.
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the effusion of CsCl vapor. The data of Carlson et al.⁸ are in agreement with the line drawn according to equation (17) with a value of unity for B. The data of Wey and Wahlbeck⁹ are seen to have a linear dependence on $\delta\bar{\omega}(0)/2\pi$. The data of Wey and Wahlbeck plotted in Figure 4 were calculated as if no dimer of CsCl(g) were present. The intercept which is at 1.055 and the slope which is steeper than that given by equation (17) may be due to errors in the vapor pressure data of Treadwell and Werner¹⁰ and Kelley¹¹ and to changes in the amount of dimer present in the CsCl vapor. The steeper slope also may be

- (10) W.D. Treadwell and W. Werner, *Helv. Chim. Acta* 36, 1436 (1953).

- (11) K.K. Kelley, U.S. Bur. Mines Bull. 383, 39 (1935).
-

caused by non-ideality of the orifice. It is noted that in the vacuum balance measurements of Wey and Wahlbeck between $\delta\bar{\omega}(0)/2\pi$ of 0.2 and 0.5 that $N/(1/4 NCA)$ is too small. The reason for this behavior is not clear at present.

The angular distribution data, $P(\theta)_{\text{exp}} N/(1/4 NCA)$, are plotted in Figure 5 and are from $P(\theta)$ data of Wang and Wahlbeck¹

and from the line through the $\bar{N}/(1/4 \bar{N}CA)$ data Carlson et al.⁸ in Figure 4. The quantity $P(\theta) \bar{N}/(1/4 \bar{N}CA)$ is equal to $I(\theta)/(d\omega 1/4 \bar{N}CA)$, where $I(\theta)$ is the molecular intensity at angle θ through solid angle $d\omega$. The theoretical value of $P(\theta) \bar{N}/(1/4 \bar{N}CA)$ may be found by simple rearrangement of equation (15). The experimental data may be compared with the theoretical lines drawn in Figure 5. One may see that the agreement is very good to a value of $\delta\bar{\omega}(0)/2\pi$ of ca. 0.5, corresponding to a Knudsen number, λ/d , of ca. 0.4. At higher pressures the angular distributions show greater intensities in the forward direction than the theory indicates.

IV. CYLINDRICAL ORIFICES

Clausing^{12,13} derived equations for the angular distribution

(12) P. Clausing, Physica 9, 65 (1929).

(13) P. Clausing, Z. Physik 66, 47 (1930).

of molecules effusing from cylindrical orifices. There are two contributions to the number of molecules effusing:

1) molecules which pass directly through the orifice - call these class I molecules and 2) molecules which leave the orifice toward the vacuum only after one or more wall collisions - call these class II molecules. From the equations given by Clausing¹³, it is possible to calculate theoretical angular distributions for both classes of molecules.

The nature of corrections necessary when λ becomes very small can be seen from Figure 6.

The Clausing¹³ distribution for class I molecules is simply the cosine law of effusion, as given by equation (6), multiplied by a cut-off function. The cut-off function is required because when $\theta \neq 0$ the entire orifice area is not open for trajectories of class I molecules. For the molecular flow region with gas phase collisions, this treatment for class I molecules must be correct because of its dependence on the cosine law of

effusion which has been experimentally validated¹. For the transition region, this distribution for class I molecules will be modified in the same way as previously done for the ideal orifice in equation (15); i.e.,

$$dN_{\theta}^I = (dN_{\theta}^I)_{\text{Clausing}} [1 + \cos \theta (\delta \bar{\omega}(0)/2\pi)]. \quad (18)$$

For class II molecules, Clausing¹¹ assumed that the molecules returned to the gas-phase from the locus of their wall collisions obeying the "cosine law of restitution." The validity of this assumption has been questioned by Winterbottom, Ruth, and Hirth¹⁴⁻¹⁶ and by Wang and Wahlbeck² because no experimental

(14) W.L. Winterbottom and J.P. Hirth, J. Chem. Phys. 37, 784 (1962).

(15) V. Ruth, W.L. Winterbottom, and J.P. Hirth, Z. angew. Phys. 16, 53 (1963).

(16) W.L. Winterbottom, J. Chem. Phys. 47, 3546 (1967).

measurements have yet agreed with the Clausing angular number distribution. Thus, dN_{θ}^{II} will represent the correct angular distribution component from the wall.

For class II molecules, it is assumed that all molecules which strike the orifice wall are restituted according to the dN_{θ}^{II} distribution. The number of molecules which strike the orifice wall, N_{II} , is now desired. This will be the number of molecules which pass through the gas-side opening of the orifice minus those which pass through the vacuum-side opening of the orifice; see Figure 6. Equation (15) appropriate for the ideal orifice may be applied to both openings. Thus,

$$N_{II} = N \bar{C} A \left\{ \int_0^{\pi/2} \cos \theta d\omega \left[1 + \cos \theta (\delta \bar{\omega}(0)/2\pi) \right] - \int_0^{\pi/2} \cos \theta d\omega R(\theta) \left[1 + \cos \theta (\delta \bar{\omega}(0)/2\pi) \right] \right\}. \quad (19)$$

Rearranging equation (19) gives

$$N_{II} = N \bar{C} A \left\{ \int_0^{\pi/2} \cos \theta d\omega [1 - R(\theta)] + \int_0^{\pi/2} \cos^2 \theta d\omega \left[(\delta \bar{\omega}''(0)/2\pi) - R(\theta)(\delta \bar{\omega}(0)/2\pi) \right] \right\}. \quad (20)$$

The first integral of equation (20) is the number of molecules colliding with the wall in the Clausius theory; thus,

$$N_{II}/N_{II}^{\text{Clausius}} = 1 + \frac{\int_0^{\pi/2} \cos^2 \theta d\omega \left[(\delta \bar{\omega}''(0)/2\pi) - R(\theta)(\delta \bar{\omega}(0)/2\pi) \right]}{\int_0^{\pi/2} \cos \theta d\omega [1 - R(\theta)]}. \quad (21)$$

The wall distribution can be expressed as

$$dN_{\theta}^{II} = (dN_{\theta}^{II}, MF) N_{II}/N_{II}^{\text{Clausius}}. \quad (22)$$

The angular number distribution for the cylindrical orifice is given by the sum of dN_{θ}^I and dN_{θ}^{II} ;

$$dN_{\theta} = (dN_{\theta}^I)_{\text{Clausius}} \left[1 + (\delta \bar{\omega}(0)/2\pi) \cos \theta \right] + (dN_{\theta}^{II}, MF) \left[1 + \frac{\int_0^{\pi/2} \cos^2 \theta d\omega \left[(\delta \bar{\omega}''(0)/2\pi) - R(\theta)(\delta \bar{\omega}(0)/2\pi) \right]}{\int_0^{\pi/2} \cos \theta d\omega [1 - R(\theta)]} \right]. \quad (23)$$

Experimental angular distributions may be compared with the above distribution using the experimental data of Adams et al.¹⁷

(17) J.Q. Adams, T.E. Phipps, and P.G. Wahlbeck, J. Chem. Phys. 49, 1609 (1968). For data in tabular form, see J.Q. Adams, Ph.D. thesis, University of Illinois, Urbana, Illinois, 1961.

In this comparison, one must calculate the

theoretical distribution from equation (23) ; $R(\theta)$ was assumed to be the same as $R(s)_{x=0}$ of Clausing^{13,*}.

(*) Clausing¹³ derived that

$$R(s)_{x=0} = (2/\pi) \cos^{-1} p - (2p/\pi) \sqrt{1 - p^2},$$

where $p = \ell/2r \tan \theta$. When $p > 1$, set $R(s)_{x=0} = 0$.

In Figure 7 may be seen a comparison between the theoretical values of dN_θ/dN_0 and the experimental values of I_θ/I_0 for the long cylindrical orifice ($\ell/d = 1.39$) of Adams et al.¹⁷ plotted vs. $\log Z$, where Z is the number of wall collisions $\text{cm}^{-2} \text{sec}^{-1}$, a quantity dependent on pressure/ $\sqrt{T}$. In this case, dN_θ^{II} values were selected so as to give the best agreement between theory and experiment. It is to be noted that the agreement of experimental data with equation (23) is very good to a value of $\log Z$ of 19.6 which corresponds to a Knudsen number of ca. 0.4. The deviation of the experimental data from the theory at higher pressures is toward a greater intensity in the forward direction as was also true in the near-ideal orifice case, see Figure 5.

In Figure 8 may be seen the theoretical values of dN_θ/dN_0 plotted vs. $\log Z$ for the short cylindrical orifice ($\ell/d = 0.496$) of Adams et al.¹⁷ A comparison with the experimental data of Adams is inconclusive.)

→ The theory would indicate that the isotropy failure characteristics of class I molecules approximately balance out the small λ characteristics of class II molecules so that the total dN_θ/dN_0 does not show a strong dependence on pressure.

V. DISCUSSION.

The theory for the transition region presented in this paper has as its basis a molecular model. Therefore, it is related most closely to the molecular flow region as treated by the kinetic theory of gases. Carlson et al.^{8,*}

(*) There is a typographical error in equation (7)⁸ for adiabatic hydrodynamic flow; it should read

$$\left(\frac{dw}{dt}\right)_a = \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{2(\gamma-1)}} \left(\frac{\gamma m}{kT}\right)^{\frac{1}{2}} S_2 P.$$

have discussed previously the fluid flow theory for the hydrodynamic flow region and the empirical equation developed by Knudsen¹⁸ for all of his experimental data.

(18) M. Knudsen, Ann. Physik 28, 909 (1909).

The effects on the angular number distribution data for the ideal orifice and the long non-ideal orifice in the transition region are opposite; $P(\theta)$ increases with increasing pressure for the ideal orifice, but $P(\theta)$ decreases with increasing pressure for the long non-ideal orifice. The theory for the transition region gives satisfactory explanations for these effects for the ideal orifice, Figure 5, and for the long non-ideal orifice, Figure 7, for Knudsen numbers greater than 0.4. In addition, the theory satisfactorily explains the orifice transmission factor data for the ideal orifice, Figure 4.

Integration of equation (23) for the cylindrical orifice should provide theoretical orifice transmission factor data. In a future paper, these calculated orifice transmission factors will be compared with experimental data.

The theory for the transition region presented in this paper should be capable of expansion to other non-ideal orifice shapes; e.g., the conical orifice.

In Table I, limits in terms of λ or K separating the transition region from the molecular flow region and the

hydrodynamic flow region were given. These limits were determined by investigators finding the λ or K values at which deviations were noted from molecular flow or hydrodynamic flow results. The true nature of these limits may be noted from Figures 4 and 5; the changes in flow characteristics are continuous functions of λ . The limits which a particular investigator finds from his experiments depends upon the sensitivity which he has for detecting changes in his experimental results. This is the probable explanation for the variation in values of the limit between the molecular flow and the transition region for the ideal orifice; see data tabulated by Wang and Wahlbeck¹.

In the theory developed here, $\delta\bar{\omega}(0)/2\pi$ plays an important role. It is given mathematically by equation (13) and is a function of r/λ . It is noted that r/λ is $\frac{1}{2K}$ where K is the Knudsen number. Thus, the Knudsen number appears to have theoretical significance.

With the equations which have been developed; e.g., for the ideal orifice, equations (15) and (17), and for the non-ideal orifice, equation (23) and its integrated form, it should be possible to calculate equilibrium vapor pressures from effusion data acquired in the transition region.

Because the effusion intensities are related to $\delta\bar{\omega}(0)/2\pi$, it should be possible to extract information from effusion data regarding $\delta\bar{\omega}(0)/2\pi$ and, more importantly, regarding λ and molecular diameters.

VI. ACKNOWLEDGMENTS.

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As a graduate student, the author had several discussions concerning effusion with Professor T.E. Phipps of the University of Illinois, Urbana, Illinois, and Dr. J.Q. Adams. Some of the ideas presented here grew from those discussions.

CAPTIONS FOR FIGURES.

- Figure 1. Molecules are members of the " $\delta\omega$ molecular group" if their trajectories lie in $\delta\omega$. Sources for members of the $\delta\omega$ molecular group are represented by "S" mechanisms, and terminations for members are represented by "R" mechanisms. The region of space at $\underline{0}$ is isotropic if the number of molecules in the $\delta\omega$ molecular group moving toward $\underline{0}$ in $\delta\omega_L$ and $\delta\omega_R$ are equal and those moving away from $\underline{0}$ in $\delta\omega_L$ and $\delta\omega_R$ are equal.
- Figure 2. Illustration used for derivation of angular number distribution for the ideal orifice; i.e., the cosine law of effusion.
- Figure 3. Illustration used for effusion at $\theta = 0$. At the collision site at a distance from the orifice between L and $L+dL$, the ideal orifice subtends a solid angle represented by a cone with a half-angle ψ .
- Figure 4. Near-ideal orifice transmission factors, N ($1/4 N\bar{C}A$), plotted vs. the isotropy failure parameter, $\delta\bar{\omega}(0)/2\pi$. Values of Knudsen numbers are given on the upper scale. The theory, equation (17) with $B = 1$, predicts a linear dependence given by the indicated line. See text for discussion.
- Figure 5. Near-ideal orifice angular number distributions, $P(\theta) N / (1/4 N\bar{C}A)$, plotted vs. the isotropy failure parameter, $\delta\bar{\omega}(0)/2\pi$. Values of the Knudsen number are given on the upper scale. The lines are based on equation (15) with $B = 1$, whereas the points are experimental. The theory fits the experimental data well on the left-hand side of the figure. Experimental data are not plotted for $\theta = 20^\circ$; the agreement between those data and the theoretical line is similar to that for $\theta = 0$.

Figure 6. Illustration used for effusion at $\theta = 0^\circ$ through a non-ideal cylindrical orifice of length ℓ with a radius r . At a collision site a distance L inside the effusion vessel, the vacuum opening of the orifice subtends a solid angle $\delta\omega$, and the orifice wall subtends a solid angle $\delta\omega'$.

Figure 7. Angular number distributions for a long cylindrical orifice ($\ell/d = 1.39$). The theoretical data, dN_θ/dN_0 (normalized by $\theta = 0$ values), are indicated by the solid lines. The experimental data of Adams et al.¹⁷, $\frac{I(\theta)}{I(0)}$, are plotted as points. The abscissa is $\log Z$, where Z is the number of wall collisions $\text{cm}^{-2} \text{ sec}^{-1}$, a quantity proportional to $P/\sqrt{T}$. See text for a discussion of the figure.

Figure 8. Angular number distributions for short cylindrical orifice ($\ell/d = 0.496$). The theoretical data, dN_θ/dN_0 (normalized by $\theta = 0$ values), are indicated by the solid lines. The abscissa is $\log Z$, where Z is the number of wall collisions $\text{cm}^{-2} \text{ sec}^{-1}$, a quantity proportional to $P/\sqrt{T}$.

Figure 1.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Appendix 4

Effusion. VIII. Orifice Transmission Probabilities as a
Function of Pressure for a Near-Ideal and for Right-Circular
Cylindrical Orifices

by

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Effusion. VIII. Orifice Transmission Probabilities as a Function of
Pressure for a Near-Ideal and for Right-Circular Cylindrical Orifices*

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(*) Based on a thesis by S. J. Wey submitted in partial fulfillment of the requirements for the Ph. D. degree, Illinois Institute of Technology, Chicago, Illinois, 1971.

Abstract:

Orifice transmission probabilities (defined as the ratio of the number of molecules leaving an orifice into vacuum to the number of molecules entering the orifice from a gas container according to the kinetic theory of gases) have been determined for 15 orifices with length to diameter ratios from 0.02 to 9.53, with a pressure of CsCl vapor from 3.7×10^{-3} torr to 1.826 torr corresponding to values of the Knudsen number (ratio of mean free path to orifice diameter) from 17.6 to 0.051. Total effusion measurements have been made using both a multiple cell effusion method and a vacuum balance apparatus. The data agree well with previous experimentally determined values, with Clausing orifice transmission probabilities for large K calculated by Demarcus, and with values calculated from equations derived by Wahlbeck. It is now possible to calculate vapor pressures from transition region data provided the molecular diameter is known.

INTRODUCTION

The transmission probability, W , of an effusion orifice may be defined as the number of molecules second⁻¹ exiting from an orifice divided by the number of molecules passing through the entrance plane of the orifice second⁻¹; i.e., from the kinetic theory $\frac{1}{4} N \bar{C} A$, where N is the number of molecules cm⁻³ of gas inside the effusion cell (gas container), $\bar{C}$ is the average velocity, and A is the cross-sectional area of the orifice. If the number of molecules sec⁻¹ leaving the effusion cell is η , then the definition gives

$$W = \eta / \frac{1}{4} N \bar{C} A. \quad (1)$$

In terms of the mass sec⁻¹ leaving the effusion cell, $\dot{G}$, W may be written as

$$W = \dot{G} / \frac{1}{4} N \bar{C} A m, \quad (2)$$

where m is the mass per molecule of the effusing species. If there is more than one effusing species, equations such as (1) and (2) can be written for each species.

The parameter W will be a function of the geometry of the orifice; i.e., its shape and dimensions. There have been a number of discussions¹⁻⁸ of the geometrical dependence of W in which useful tables of values of

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- (1) P. Clausing, Koninkl. Ned. Wetenschap. Proc. 35, 1023 (1926).
 - (2) P. Clausing, Physica 9, 65 (1929).
 - (3) P. Clausing, Z. Physik 66, 471 (1930).
 - (4) P. Clausing, Ann. Physik Ser. 5, 12, 961 (1932).

- (5) W. C. DeMarcus, Rept. K-1302, Oak Ridge Gaseous Diffusion Plant, 1957.
 - (6) R. D. Freeman and J. G. Edwards, in Condensation and Evaporation of Solids, E. Rutner, P. Goldfinger, and J. P. Hirth, Eds. (Gordon & Breach, New York, 1964), p. 127.
 - (7) R. D. Freeman and J. G. Edwards, in The Characterization of High Temperature Vapors, J. L. Margrave, Ed. (John Wiley & Sons, Inc., New York, 1967), p. 508.
 - (8) R. P. Iczkowski, J. L. Margrave, and S. M. Robinson, J. Phys. Chem. 67, 229 (1963).
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W have been given. These theoretical values of W should be valid when λ , the mean free path, for the gas in the effusion cell is large compared to the diameter of the orifice (the molecular flow region). Through experimental studies, the parameter W has been found to be also a function of the pressure of the gas and geometry of the gaseous species. This latter dependence may be simply given through the parameter Knudsen number, K, where $K = \lambda/d$. The mean free path, λ , is a function of the pressure of the gas and molecular diameter, and d is the orifice diameter. Earlier effusion studies may be classified as measurements of angular number distributions or as measurements of orifice transmission probabilities (total effusion). Previous results have been summarized by Wang and Wahlbeck for the near-ideal orifice⁹ and for the right-circular cylindrical orifices.¹⁰

- (9) K. C. Wang and P. G. Wahlbeck, J. Chem. Phys. 47, 4799 (1967).
 - (10) K. C. Wang and P. G. Wahlbeck, J. Chem. Phys. 49, 1617 (1968).
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The flow of gases through orifices may be divided into regions whose boundaries are dependent on mean free path or Knudsen number. Such regions have been described previously by Wahlbeck;¹¹ briefly they are the mole-

- (11) P. G. Wahlbeck, J. Chem. Phys. (Accepted for Publication).
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cular flow (large K), transition, and hydrodynamic flow (small K). By introducing the dependence of W on K, one may treat the flow of gases through orifices in all three regions by equations (1) and (2). In this paper, the variation of W with K values will be discussed.

In this paper are given experimentally determined values of W for a near-ideal orifice and a series of right-circular cylindrical orifices of varying L/d values; L is the orifice length. The effusion cells in these experiments have been designed so as to be isothermal, single-oven cells. In these experiments values of W are computed by solution of equation (2), where $N = p/k T$ (p is the pressure of the gas, and T is the temperature of the gas) and $\bar{C} = \sqrt{8 k T / \pi m}$. Thus,

$$W = \dot{G} \sqrt{2 \pi k T} / (p A \sqrt{m}). \quad (3)$$

It has been customary in the Knudsen method for vapor pressure measurements to measure the mass transported through an orifice and to use equation (3) as solved for p to calculate p.

Theories for the flow of gases in the transition region have been developed by Narasimha,¹² Willis,¹³ and Wahlbeck.¹¹ Narasimha¹² developed

(12) R. Narasimha, J. Fluid Mech. 10, 371 (1961).

(13) D. R. Willis, J. Fluid Mech. 21, 21 (1965).

and equation for an ideal orifice which was

$$W = 1 + 0.125/K. \quad (4)$$

For an ideal orifice, Willis¹³ developed

$$W = 1 + 0.083 \text{ Re} + F(\text{Re}) , \quad (5)$$

where Re is the Reynolds number and $F(\text{Re})$ is a function of Re . For the ideal orifice, Wahlbeck¹¹ found that

$$W = 1 + 2/3 [\delta\bar{\omega}(0)/2\pi] , \quad (6)$$

where

$$\delta\bar{\omega}(0)/2\pi = 1 - \frac{\pi r}{2\lambda} [H_1(r/\lambda) - Y_1(r/\lambda)] + r/\lambda , \quad (7)$$

where $H_1(x)$ is a Struve function, $Y_1(x)$ is a Bessel function of the second kind, and r is the orifice radius. For cylindrical orifices, Wahlbeck¹¹ has derived an equation (equation (23)¹¹) for the angular number distribution. For W values, one must integrate this angular number distribution equation.

EXPERIMENTAL SECTION

In order to evaluate W by use of equation (3), values for the parameters in that equation must be determined. One must measure $\dot{G}$, the mass sec^{-1} leaving the effusion cell; know the mass, m , of vapor species; know the cross-sectional area, A , of the orifice; and measure the temperature of the effusion cell, T , upon which the pressure of CsCl , p , is dependent.

The effusion cell with the orifice was of a single-oven design. The designs of the effusion cell are shown in Figure 1. Two styles of bodies of the effusion cell were used; a long style was used in the multiple cell apparatus and a short style was used in the vacuum balance apparatus. The orifices were located in removable lids which were designed and fabricated to fit both body styles. All of the effusion cells were fabricated from Grade A Ni rod. A description and dimensions (at 25°C) of the near-ideal and right-circular cylindrical orifices are given in Table I. The temperature dependence of the diameter of the orifice was calculated by using a linear expansion coefficient for Ni of $1.346 \times 10^{-5} \text{ deg}^{-1}$ and for Pt of $8.99 \times 10^{-6} \text{ deg}^{-1}$.

The effusing substance in these experiments was the vapor from CsCl (s or l). This choice was made because CsCl had been used in previous studies in this series;¹⁴ in order to get data which could be combined

(14) A previous paper in this series is K. C. Wang and P. G. Wahlbeck, J. Chem. Phys. 53, 2896 (1970); references to preceding papers may be found in this paper.

with previous data, the same chemical substances were used. The vapor is known to be highly monomeric from experiments of Miller and Kusch¹⁵

Table I. Orifice Geometries and Characteristics

# ^a	L(cm) ^d	D(cm) ^d	L/d	W(DeMarcus)	W(Exptl)
1 ^b	0.0013(±0.0001)	0.05767(±0.00029)	0.02254	0.97796±.00011	0.972±0.008
2 ^{b,c}	0.00265(±0.00058)	0.05557(±0.00036)	0.04774	0.95445±.00975	0.953
3 ^c	0.01048(±0.00021)	0.05113(±0.00022)	0.20496	0.83070±.00333	0.823
4 ^{b,c}	0.02220(±0.00020)	0.05296(±0.00030)	0.41916	0.70847±.00296	0.700
5 ^c	0.03900(±0.00040)	0.05492(±0.00031)	0.71018	0.59405±.00366	0.584
6 ^{b,c}	0.04990(±0.00027)	0.05442(±0.00025)	0.91690	0.53461±.00237	0.527
7 ^{b,c}	0.07150(±0.00067)	0.05282(±0.00026)	1.3537	0.44354±.00333	0.440
8 ^c	0.10260(±0.00013)	0.05352(±0.00026)	1.9171	0.36565±.00132	0.365
9 ^{b,c}	0.12500(±0.00100)	0.05261(±0.00031)	2.3758	0.32076±.00282	0.300
10 ^{b,c}	0.15300(±0.00033)	0.05492(±0.00037)	2.7861	0.28940±.00168	0.271
11 ^c	0.17160(±0.00107)	0.05150(±0.00033)	3.3319	0.25641±.00224	0.253
12 ^c	0.19220(±0.00107)	0.05035(±0.00086)	3.8172	0.23301±.00279	0.227
13 ^c	0.22500(±0.00167)	0.05175(±0.00024)	4.3479	0.21200±.00188	0.203
14 ^{b,c}	0.2500(±0.0010)	0.05183(±0.00035)	4.8233	0.19625±.00157	0.186
15 ^c	0.52060(±0.00013)	0.05461(±0.00014)	9.5335	0.11388±.00027	0.107

Notes:

- (a) Orifice 1 was made using Pt foil attached to a Ni body. The orifice was made by drilling a hole in the Pt foil. For orifices 2 through 15, the orifices were directly drilled in the Ni wall of the orifice cap.
- (b) Vacuum balance experiments
- (c) Multiple effusion cell experiments
- (d) Length and diameter were measured at 25°C either with a microscope or a micrometer.

(15) R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).

and Berkowitz and Chupka.¹⁶ Thermochemical data for CsCl(g) and $\text{Cs}_2\text{Cl}_2\text{(g)}$

(16) J. Berkowitz and W. A. Chupka, J. Chem. Phys. 29, 653 (1958).

have been summarized in the JANAF Thermochemical Tables.¹⁷ Equations for

(17) JANAF Thermochemical Tables, D. R. Stull, Ed. (The Dow Chemical Co. Midland, Michigan). Tables for CsCl(g) and $\text{Cs}_2\text{Cl}_2\text{(g)}$ are dated 30 June 1968.

the calculation of the vapor pressure and λ values have been given previously.⁹

The temperatures of the effusion cells were measured using a Chromel-P-Alumel thermocouple which had been calibrated at the melting points of standard samples (NBS) of Pb (327.4°C), Zn (419.5°C), and Al (659.7°C) and the melting point of pure Ag (960.8°C). Temperatures measured by the thermocouples were correct within 0.5° without any correction.

The experiments were performed with two apparatuses: (1) a multiple effusion cell apparatus and (2) a vacuum balance apparatus. These two types of experiments will be described in the following paragraphs.

In the multiple cell apparatus, fourteen effusion cells numbered 2 through 15 in Table I were set in pure alumina cell holders into holes in a large Mo block to assure that all cells were at the same temperature. The Mo block and the effusion cells were placed in a large alumina tube suspended in a resistively heated furnace equipped with a saturable-core reactor controller. This arrangement in addition to radiation shields assured an isothermal zone for all effusion cells. Mass losses of the effusion cells during a fixed time

were determined by balance measurements before and after the experiment with an Ainsworth Semi-Micro balance, Type TX, which had a sensitivity of 0.01 mg. Further details of the apparatus and experimental procedures have been described by Macur et al.¹⁸ The effusion of CsCl was regulated;

(18) G. J. Macur, R. K. Edwards, and P. G. Wahlbeck, J. Phys. Chem. 70, 2956 (1966).

i.e., the starting and stopping of the flow of CsCl through the orifice, by admitting to the apparatus Ar to a pressure ca. 0.7 atm. This was an effective regulator until the pressure of CsCl(g) exceeded 0.1 torr. Apparently at pressures greater than 0.1 torr, diffusion becomes an effective transport mechanism, and the experimental techniques are not operable. Duration of the effusion of CsCl was measured with an electric stop clock.

In the vacuum balance apparatus, the same type of experiments were performed as were done by Carlson et al.¹⁹ With the vacuum balance, the

(19) K. D. Carlson, P. W. Gilles, and R. J. Thorn, J. Chem. Phys. 38, 2725 (1963).

mass of the effusion cell was measured directly as a function of time, and $\dot{G}$ was determined readily. The effusion cell was suspended in the center of an inductively heated susceptor, in the middle of an isothermal zone. The temperature of the effusion cell was estimated by having the same thermocouple that was used in the multiple cell apparatus mounted in a quartz tube in the center of the susceptor 0.3 cm below the effusion cell. The power to the induction heater was regulated, and the power from the induction heater was hand controlled. The details of the design of the vacuum balance have been described by Suzuki and Wahlbeck.²⁰

(20) A. Suzuki and P. G. Wahlbeck, J. Phys. Chem. 70, 1914 (1966).

RESULTS

The experimental data of orifice transmission probabilities W ,
for the different orifices are given in Figures 2 and 3. [†] Values of W

(†) For tables of experimental orifice transmission probabilities, see
S. J. Wey, Ph. D. thesis, Illinois Institute of Technology, Chicago,
Illinois, 1971.

were based on equation (3) using experimentally determined data and were
plotted vs. $\delta\bar{\omega}(0)/2\pi$ (see equation (7)), a parameter discussed by Wahlbeck.¹¹
Figure 3 was used to avoid confusing overcrowding of Figure 2. General
trends in the data with orifice length and with $\delta\bar{\omega}(0)/2\pi$ may be summarized
properly from Figure 2. Also plotted on these figures are theoretical
curves as calculated from equation (4) based on Narasimha's¹² theory,
equation (5) based on Willis's¹³ theory, and equation (6) based on Wahlbeck's¹¹
theory for the ideal orifice. The theoretical lines for the right-circular
cylindrical orifices are based upon integration of the angular number dis-
tribution equation of Wahlbeck¹¹ for the cylindrical orifices which uses
the basic angular number distribution theory of Clausing.² The agreement
of the experimental data with the theoretical curves will be discussed
later in this paper.

An error analysis was performed on the values of W as determined in
the vacuum balance experiments. The probable error in temperature was
estimated to be 0.5° , the dependence of P on T was assumed from the vapor
pressure equation, and the relative error in $\dot{G}$, the rate of mass loss, was
estimated to be 1.9%. These lead to an expected relative error in W of
2.5%; this is in accord with the scatter in the data observed in Figures
2 and 3.

An error analysis was performed on the calculated values of $\delta\bar{\omega}(0)/2\pi$;

these values are a function of r/λ . Scatter in a set of data would be dependent on the uncertainty in T . The value of T with its uncertainty leads to values of $\delta\bar{\omega}(0)/2\pi$ with its uncertainty for values of K : $K = 10$, $\delta\bar{\omega}(0)/2\pi = (4.54 \pm 0.08) \times 10^{-2}$; $K = 1$, $\delta\bar{\omega}(0)/2\pi = 0.303 \pm 0.004$; $K = 0.1$, $\delta\bar{\omega}(0)/2\pi = 0.817 \pm 0.003$. The largest error in the $\delta\bar{\omega}(0)/2\pi$ values is in the middle of the range at 0.5 with a relative error of 1.2%. The range in values caused by the uncertainty in T decreases as $\delta\bar{\omega}(0)/2\pi$ goes to 0 and to 1 from 0.5.

The intercept of the W values at $\delta\bar{\omega}(0)/2\pi = 0$ in Figures 2 and 3 also may be compared with orifice transmission probabilities theoretically calculated by DeMarcus;⁵ see Table I. The theoretical values W_{DeMarcus} depend upon the uncertainties in the dimensions of the orifices; L and r . These uncertainties and the calculated uncertainties in W_{DeMarcus} are given in Table I. It is to be noted that the calculated and experimental values agree within the cited errors except for orifices 9 and 10.

Since the effusion method is usually used to determine vapor pressures, the near-ideal orifice data are plotted in Figure 4 vs. $1/T$. These vapor pressure data were calculated firstly assuming a constant orifice transmission coefficient of 0.978. Secondly, an orifice transmission factor was calculated from the equations of Wahlbeck.¹¹ In this case, W is a function of p , orifice geometry, and molecular size. Because W is a function of p , a method of successive approximations was used to calculate p ; these recalculated values of p are also plotted in Figure 4. These calculated pressures are shown from Figure 4 to be in good agreement with the pressures reported by Treadwell and Werner²¹ (solid CsCl) and compiled by Kelley²² (liquid CsCl) with an average relative

(21) W. D. Treadwell and W. Werner, *Helv. Chim. Acta* 36, 1436 (1953).

(22) K. K. Kelley, *U. S. Bur. Mines Bull.* 383, 39 (1935).

deviation of 2.5%. Kelley²² analysed available vapor pressure data for $\text{CsCl}_{(l)}$ and concluded that the best data were vapor pressures measured by quasi-static methods used by Fiock and Rodebush²³ and by von Wartenburg and Schulz.²⁴ It is to be noted that these are not effusion measurements.

(23) E. F. Fiock and W. H. Rodebush, *J. Am. Chem. Soc.* 48, 2522 (1926).

(24) H. von Wartenburg and H. Schulz, *Z. Electrochem.* 27, 568 (1921).

DISCUSSION

The experimental values of the orifice transmission probabilities for the near-ideal orifice (Pt-foil) are plotted in Figure 2. The values determined in this study using CsCl vapor agree within experimental error with values determined by Carlson et al.¹⁹ using Hg vapor. These experimental values may be compared with values determined by Liepmann²⁵ for

(25) H. W. Liepmann, J. Fluid Mech. 10, 65 (1961).

a thin-edged orifice using permanent gases; Liepmann's graphically presented values are in qualitative agreement with the values reported in this work.

In the case of these vacuum balance measurements, there are two potential difficulties caused (1) by the baffle inside the effusion cell and (2) by the hot susceptor outside the effusion cell. With regard to the first, it has been shown by Ward et al.²⁶⁻²⁸ that the internal design

(26) J. W. Ward, R. N. R. Mulford, and M. Kahn, J. Chem. Phys. 47, 1710 (1967).

(27) J. W. Ward, R. N. R. Mulford, and R. L. Bivins, J. Chem. Phys. 47, 1718 (1967).

(28) J. W. Ward, J. Chem. Phys. 47, 4030 (1967).

and chemical interactions of an effusion cell are important in determining angular number distributions of effusing molecules and consequently the orifice transmission probabilities. This effect should be most important at very low pressures of CsCl. With regard to the second, it is possible that a small pressure of CsCl could be built up in the susceptor causing some backward flow of CsCl. Both of these effects would lead to orifice transmission probabilities which would be too small. Since there is

nothing detectably incorrect with the data, it is assumed that these two effects are not causing significant errors in this experiment.

The near-ideal orifice transmission probabilities may be compared with the theoretical predictions of Narasimha,¹² Willis,¹³ and Wahlbeck¹¹ as given in Figure 2. The experimental values appear to be in best agreement with the theoretical equation given by Wahlbeck.¹¹ The general form of the dependence of W on the Knudsen number appears to be correctly given by $\delta\bar{\omega}(0)/2\pi$. Small deviations appear at values of $\delta\bar{\omega}(0)/2\pi$ larger than 0.5 which corresponds to a Knudsen number less than 0.4. The general form of the dependence of W on Knudsen number does not appear to be correctly given by the equations of Narasimha¹² and Willis.¹³

The cylindrical orifice transmission probabilities determined in this study given in Figures 2 and 3 may be compared with the theoretically predicted W values of Wahlbeck.¹¹ The agreement with the theoretical values appears to be within the experimental error for values of $\delta\bar{\omega}(0)/2\pi < 0.5$ except for orifices 9 and 10.

In conclusion, the equations of Wahlbeck¹¹ appear to fit satisfactorily the orifice transmission probabilities for the orifices experimentally investigated in this study for values of $\delta\bar{\omega}(0)/2\pi < 0.5$ corresponding to a Knudsen number greater than 0.4.

The molecular flow values of W (obtained from Figures 2 and 3 at $\delta\bar{\omega}(0)/2\pi = 0$) and values of W calculated by DeMarcus⁵ are given in Table I. The agreement between the experimental and theoretical values is excellent except for orifices 9 and 10 for which the theoretical W is slightly larger than the experimental value with no obvious reason for the discrepancy. The general agreement supports the theoretically calculated W values of DeMarcus.⁵

For the users of the Knudsen effusion method for calculating vapor pressures, the application of the equations given by Wahlbeck¹¹ offers the possibility of extending measurements to vapor pressures higher than what was believed to be possible previously. The data given in Figure 4 illustrate the extension of the Knudsen method well into the transition region. Agreement of these vapor pressures with independently determined values is very good with an average relative deviation of 2.5%.

The data presented in this paper appear to have smooth dependencies on $\delta\omega(0)/2\pi$. There are no erratic changes in W . In an earlier study in this series, Wang and Wahlbeck¹⁰ found that $P(\theta)$, the probability density for effusion at θ , for cylindrical orifices, mounted on a double-oven effusion cell, were dependent on the temperature differences between the front and back ovens. Storms²⁹ has commented on complications pre-

(29) E. Storms, High Temp. Sci. 1, 456 (1969).

sented when a temperature gradient occurs in an effusion cell. The smooth behavior in the present data are probably related to the fact that the effusion cell was very nearly isothermal.

In the studies of angular number distributions, normalization of the data must be done. The normalization procedures which have been used are (1) to normalize $I(\theta)$ data with $I(\theta = 0)$ or (2) to normalize $I(\theta)$ with the total number of effusing molecules and create a probability density function, $P(\theta)$.⁹ The latter procedure is the one which has been used in previous papers in this series.^{14,11} It has been pointed out⁹ that ideally one wishes $I(\theta)_{\text{exptl}}/I(\theta)_{\text{ideal orifice}}$, and this ratio may be computed by

$$I(\theta)_{\text{exptl}}/I(\theta)_{\text{ideal orifice}} = [P(\theta)_{\text{exptl}}/P(\theta)_{\text{ideal}}]^W. \quad (8)$$

With values of W based on this work, values for $I(\theta)_{\text{exptl}}/I(\theta)_{\text{ideal orifice}}$ may be evaluated from angular distribution data.

ACKNOWLEDGMENTS

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CAPTIONS FOR FIGURES

Figure 1 - Design of the effusion cells. The long style (left) was used in the multiple cell experiments. The short style (right) was used in the vacuum balance apparatus. The caps (containing the orifices) were fabricated to fit both cell body designs. Material was Ni except for the Pt-foil orifice.

Figure 2 - Orifice transmission probabilities plotted vs. $\delta\bar{\omega}(0)/2\pi$.

"Vacuum balance measurements" is abbreviated as V. B. M. "Multiple effusion measurements" is abbreviated as M. E. M.

Figure 3 - Orifice transmission probabilities plotted vs. $\delta\bar{\omega}(0)/2\pi$.

"Vacuum balance measurements" is abbreviated as V. B. M. "Multiple effusion measurements" is abbreviated as M. E. M.

Figure 4 - Vapor pressure of CsCl plotted vs. $10^3/T^\circ\text{K}$. The melting point of CsCl is at 915°K . The open circle points are vapor pressures using a constant orifice transmission probability of 0.978 (Pt-foil orifice). The closed triangle points were calculated using calculated orifice transmission probabilities indicated by the dashed line on Figure 2; a successive approximation method was used. The lines are vapor pressure data by Treadwell and Werner²¹ and by Kelley.²²

Figure 1

Multiple Effusion Cell

Cell Body for Vac. Baln. Meas.

"Pt-foil" Near-Ideal Effusion Cell

Figure 2

Figure 3

Figure 4

Appendix 5

Vapor Pressures and the Standard Enthalpy Change for Sublimation of $\text{Ti(s,}\beta\text{)}$

by

Hung Yuan Wu and P. G. Wahlbeck

High Temp. Sci. (submitted)

COO-1029-38

Vapor Pressures and the Standard Enthalpy Change for Sublimation of Ti(s, β)

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ABSTRACT

The sublimation of Ti(s, β) has been examined (1) by performing a mass spectrometric analysis of the equilibrium vapor and (2) by Knudsen vapor pressure determinations. The mass spectrometric analysis showed Ti(g) to be the predominant species with $P_{\text{Ti}_2}/P_{\text{Ti}} < 0.0028$. There was no systematic dependence of the Knudsen vapor pressures on orifice area leading one to conclude that the sublimation coefficient is unity. These Knudsen vapor pressure measurements are in good agreement with earlier Langmuir vapor pressure measurements performed by Edwards, Johnston, and Ditmars. A recommended $\Delta H_{298, \text{subl}}^\circ$ for Ti(s, β) of 111.847 ± 0.411 kcal / g-atom results from a combination of the data of the present study and of the study of Edwards et al.; for the combined data there are excellent agreements between values determined by second- and third- law treatments.

INTRODUCTION

There have been several previous studies of the vapor pressure of $\text{Ti(s},\beta)$ which enable one to calculate $\Delta H_{298,\text{sublimation}}^\circ$ for $\text{Ti(s},\beta)$. The previous studies have been summarized by Nesmeyanov,¹ by Honig and Kramer,² by Stull in the JANAF tables,³ and by Hultgren, et al.⁴

All of the previous measurements of the vapor pressure of $\text{Ti(s},\beta)$, those by Blocher and Campbell;⁵ by Carpenter and Mair;⁶ by Edwards, Johnston, and Ditmars;⁷ by Morrison;⁸ by Kuz'min and Palatnik;⁹ and by Strassmair and Stark,¹⁰ have used the Langmuir free evaporation technique. The titanium sample was either in the form of a block⁷ or in the form of a filament.^{5,6,8-10} In these studies using the Langmuir method, the following assumptions were made: (1) the vapor species was assumed to be Ti(g) , (2) the vaporization coefficient was assumed to be unity, and (3) the emissivity of the Ti sample must be assumed in order to ascertain temperatures from optical pyrometer measurements in all studies but that by Edwards et al.⁷ In the study by Edwards et al.,⁷ the temperature of the Ti block was measured through the use of a blackbody cavity; also the emissivity of $\text{Ti(s},\beta)$ was measured so that corrections of temperatures in previous Langmuir studies could be made.

Ivanov and Kudryavtsev¹¹ reported a study of the influence of the pressure of residual gases in the vacuum on the vapor pressure of $\text{Ti(s},\beta)$. They found that on decreasing the pressure from 5×10^{-5} torr to 1×10^{-7} torr that $\Delta H_{298,\text{subl}}^\circ$ increased from 102.85 kcal/g-atom to 107.12 kcal/g-atom.

The research reported in this paper was designed to consider or to remove the assumptions listed above which had been used in the previous Langmuir studies. The vapor species were identified directly through a mass spectrometric investigation. The vapor pressure measurements were performed

using a different technique, the Knudsen method. In the Knudsen method, the evaporating sample is contained in an "effusion cell," and the temperature of this enclosure may be determined by sighting an optical pyrometer on a blackbody cavity; the emissivity assumption is avoided. By variation of orifice size, the vaporization coefficient may be evaluated; see Motzfeldt.¹² The vapor pressure measurements have been used to evaluate $\Delta H_{298, \text{subl}}^\circ$ of Ti(s, β).

EXPERIMENTAL SECTION

Samples.- The samples of Ti used in this research were from a bar of "iodide" titanium with a stated purity of 99.999% obtained from the Research Organic/Inorganic Chemical Company of Sun Valley, California. Small chips of the Ti metal were produced by using a lathe with a cutting tool. The Ti chips were subsequently washed with water and reagent grade acetone.

Mass Spectrometry.- The vapor species in equilibrium with solid titanium were identified by mass spectrometry. The basic mass spectrometer was a Bendix time-of-flight instrument, model number 12-107. This mass spectrometer is equipped so that oscilloscopic observations of the mass spectrum can be made or so that ion intensities can be recorded with a Leeds and Northrup recorder.

The sample of solid titanium was contained in an outgassed W Knudsen cell, fabricated from swaged W rod using tungsten carbide tools, which was heated by electron bombardment. The design of the high temperature Knudsen cell assembly was similar to that of Chupka and Inghram.¹³ Electric field plates for deflection of ions originating from the Knudsen cell assembly were used.

The temperature of the effusion cell was measured with a disappearing filament Leeds and Northrup optical pyrometer. The orifice as an opening to the interior of the effusion cell was used as a blackbody source.

To identify the parent vapor species, mass scans and ionization efficiency curves for the ion species were obtained.

Effusion Rate Measurements.- The rate of effusion of titanium vapor was measured using a W effusion cell differing in design from that used in the mass spectrometric studies. The effusion cell was fabricated from the same

swaged W rod stock. The crucible was supported by three W legs directly attached to the effusion cell. A blackbody hole for temperature measurements was located in the cell's base. Three removable caps containing orifices with different dimensions were made to fit the one cell body. The orifice dimensions are given in Table I. The diameter of the cavity inside the effusion cell was 0.9 cm with a height of 1.7 cm; the Ti sample was loosely lying on the bottom of the effusion cell. The effusion cell and caps were outgassed to a condition of constant mass by heating to 2100°K for 10 hours.

The effusion runs were performed in a pyrex vacuum system. Vacuum was achieved by using mercury vapor diffusion pumps backed by a mechanical pump. Liquid-nitrogen-cooled traps were located between the diffusion pumps and the effusion cell and between the diffusion pumps and the mechanical pump. Pressure in the high vacuum system was measured with a hot cathode ionization gauge. During the run, the pressure was always maintained below 5×10^{-5} torr and usually below 2×10^{-6} torr. The effusion cell was heated by eddy currents induced in the cell with power supplied by a 20 kw General Electric induction heater operated at 450 kHz.

The temperature of the effusion cell was determined by sighting on the effusion cell's blackbody hole with a Leeds and Northrup optical pyrometer. The low temperature scale of the pyrometer was calibrated by sighting on a blackbody cavity at the temperature of the melting point of Cu using a sample from the National Bureau of Standards; the melting point was reported to be 1083.3°C. The intermediate scale was calibrated through comparison of temperature readings on the two temperature scales when sightings were made on a heated lamp filament. A correction for the reflection of

Table I. Effusion Orifice Dimensions

Orifice	$D^{a,b}$	$L^{a,c}$	$2L/D$	W^d
A	0.15325 cm	0.09228 cm	1.20427	0.63144
B	0.1029	0.01909	0.37108	0.84412
C	0.08400	0.03397	0.80873	0.71564

Notes:

- (a) Dimensions measured at 25°C. The dimensions at higher temperatures were calculated using the linear coefficient of expansion of $6.1 \times 10^{-6} \text{ deg}^\circ\text{C}^{-1}$.
- (b) A microscope and micrometer scale were used to measure this dimension.
- (c) The effusion cell cap was mounted on a 45°-right angle prism. The projected length of the orifice was measured as in (b).
- (d) Orifice transmission probabilities, W , for these cylindrical orifices were calculated from equations given by W. C. DeMarcus, U. S. Atomic Energy Commission Rept. K-1302, Oak Ridge Gaseous Diffusion Plant, 1957.

radiant energy by a window and prism was calculated by measuring the temperatures of an object with and without the window and prism assembly.

It was concluded that $1/T_{\text{obs}} - 1/T_{\text{true}} = (1.554 \pm 0.194) \times 10^{-5}$.

The mass loss of the effusion cell was used to calculate the transport rate of Ti from the effusion cell. The effusion cell was weighed before and after the effusion run on an Ainsworth semi-micro balance, Type TX, which had a sensitivity of 0.01 mg.

The time of the effusion run was determined by an electric stopcock.

RESULTS

Mass Spectrometry.- A sample of Ti(s, β) was vaporized from the Knudsen cell at 1905°K in the high temperature Knudsen cell inlet of the mass spectrometer with a pressure in the vacuum of 3×10^{-6} torr.

The ions which were observed at 50 e.v. (accelerating voltage for ionizing electrons) were $\text{Ti}^+(\text{g})$ and $\text{Ti}^{++}(\text{g})$. No observation of $\text{Ti}_2^+(\text{g})$, $\text{TiO}^+(\text{g})$, or $\text{TiO}_2^+(\text{g})$ was made. The intensities of the ions were $\text{Ti}^+ : \text{Ti}^{++} : \text{Ti}_2^+ : \text{TiO}^+ : \text{TiO}_2^+ = 1.00 : 0.062 : < 0.003 : < 0.006 : < 0.006$.

The appearance potentials of $\text{Ti}^+(\text{g})$ and $\text{Ti}^{++}(\text{g})$ were determined from a linear extrapolation of ionization efficiency curves. The energy scale was calibrated using the ionization of Hg(g) to form $\text{Hg}^+(\text{g})$ with an appearance potential of 10.437 e.v.¹⁴ The ionization efficiency curves did not show any unusual breaks. The appearance potentials of $\text{Ti}^+(\text{g})$ determined from two separate ionization efficiency curves were 6.55 and 6.76 e.v. which compare favorably with the ionization potential of 6.82 e.v.¹⁴ The appearance potential of $\text{Ti}^{++}(\text{g})$ was 23.03 e.v. which is higher than the value calculated from ionization potentials of 20.40 e.v.,¹⁴ but it is in agreement with a value of 23.2 e.v. measured by Hampson and Gilles.¹⁵ From these results one concludes that $\text{Ti}^+(\text{g})$ comes from Ti(g) and that the extent of ionization of Ti(g) to form $\text{Ti}^{++}(\text{g})$ is small.

One may assume that the ionization cross section, Q , of $\text{Ti}_2(\text{g})$ is twice that of Ti(g) and that the multiplier gain, η , for $\text{Ti}_2(\text{g})$ is $1/\sqrt{2}$ that of Ti(g) (inverse square root of mass dependence). The isotopic fraction, F , of ^{48}Ti is 0.7394 and of $^{96}\text{Ti}_2$ is 0.5632. From $P_i = I_i^+ / Q_i \eta_i F_i$, the ratio of pressures of $\text{Ti}_2(\text{g})$ to Ti(g) must be less than $\frac{0.003}{1.000} \times \frac{1}{2} \times \frac{\sqrt{2}}{1} \times \frac{0.7394}{0.5632} = 0.0028/1.00$. Thus, in terms of the importance of vapor species, Ti(g) is

the most important with $\text{Ti}_2(\text{g})$ having a smaller pressure by at least a factor of 0.0028

Effusion measurements.- The effusion measurements reported here are for vapor predominantly consisting of $\text{Ti}(\text{g})$, based on the mass spectrometer results, in equilibrium with $\text{Ti}(\text{s},\beta)$. The melting point of $\text{Ti}(\text{s},\beta)$ has been reported by Schofield and Bacon¹⁶ to be $1933 \pm 10^\circ\text{K}$ and by Oriani and Jones¹⁷ to be $1945 \pm 4^\circ\text{K}$; all measurements reported in this paper are for temperatures below 1933°K .

From studies of Ti and W which have been summarized on the phase diagram of the Ti-W system,¹⁸ it is known that one may form solutions of Ti in W up to a composition of 18 atomic % Ti. In the present experiments, solid solution formation should not occur to any appreciable extent. There was very little physical contact between the chips of $\text{Ti}(\text{s},\beta)$ and the W effusion cell. The vapor originated from pure $\text{Ti}(\text{s},\beta)$ chips inside the effusion cell. The vapor pressure of $\text{Ti}(\text{g})$ inside the cell would not be effected if the W cell walls do not act as a sink for titanium vapor.

The experimentally measured quantities for a single run with a given orifice are (1) mass loss of the effusion cell, (2) temperature of the effusion cell, and (3) duration of the run. These data are tabulated in Table II. From these data, the equilibrium vapor pressure of $\text{Ti}(\text{s},\beta)$ may be calculated. The equilibrium vapor pressures of $\text{Ti}(\text{s},\beta)$ vs. $1/T^\circ\text{K}$ are plotted in Figure 1.

If there is a non-unit vaporization coefficient associated with the sublimation of $\text{Ti}(\text{s},\beta)$, the pressures calculated for the runs in which smaller orifices are used should be greater; see Motzfeldt.¹² Thus, $P_C > P_B > P_A$. From the data shown in Figure 1, it is evident that such a

Table II. Vapor Pressure and Thermodynamic Data from this Study

Run	T°K	t, min	G,mg, mass loss	$10^7 P$ (atm)	$\left(\frac{G_T^\circ - H_{298}^\circ}{T}\right)_{\text{Ti(g)}}^a$ (cal/deg g-atom)	$\left(\frac{G_T^\circ - H_{298}^\circ}{T}\right)_{\text{Ti(s,}\beta)}^a$	$\Delta H_{298, \text{subl}}^b \text{ (III),}$ (kcal/g-atom)
1A	1830	480	2.080	8.490	48.2937	15.0644	111.641
2A	1851	360	1.890	9.381	48.3439	15.1312	112.524
3A	1862	300	2.270	13.563	48.3702	15.1662	111.813
4A	1886	300	2.730	16.429	48.4275	15.2425	112.500
5A	1894	300	3.190	19.238	48.4467	15.2679	112.371
6A	1910	300	3.820	23.144	48.4841	15.3179	112.595
							Ave: 112.241±0.372 ^c
2B	1911	390	4.220	35.888	48.4864	15.3210	110.987
3B	1885	480	3.305	22.685	48.4251	15.2393	111.233
4B	1919	460	5.050	36.479	48.5049	15.3457	111.377
5B	1873	606	3.116	16.890	48.3965	15.2011	111.641
6B	1863	851	3.712	14.29	48.3726	15.1693	111.678
7B	1909	480	4.369	30.170	48.4818	15.3148	111.532
8B	1850	900	3.300	11.973	48.3415	15.1280	111.568
							Ave: 111.431±0.322 ^c
2C	1923	650	3.860	34.988	48.5141	15.3581	111.763
4C	1898	800	2.930	21.444	48.4562	15.2806	112.193
6C	1904	760	2.770	21.372	48.4702	15.2994	112.551
							Ave: 112.169±0.322 ^c
							Overall Ave: 111.873±0.511 ^c

Table II. Vapor Pressure and Thermodynamic Data from this Study (continued)

- (a) From "JANAF Thermochemical Tables"³
- (b) See note (a) of Table III.
- (c) Standard deviation.

relationship does not exist. Within the scatter in the experimental data, the vaporization coefficient is unity.

Also tabulated in Table II are the free-energy functions, $\frac{G_T^\circ - H_{298}^\circ}{T}$, for Ti(g) and Ti(s, β) used in the calculation of the "third-law " standard enthalpy change for sublimation. The thermodynamic data associated with the sublimation of Ti(s, β) are summarized in Table III from this research and from previous investigations. Also included in Table III is a treatment for the combined set of data from this study and from Edwards et al.⁷ This combined set of data has a more extensive temperature range than either set alone.

Table III. Summary of Thermodynamic Results for Sublimation of Ti(s,β)

Investigators ^g	$\frac{\Delta H_{298}^{\circ} \text{ (3rd law)}^a}{\text{kcal (g-atom)}^{-1}}$	$\frac{\Delta H_{298}^{\circ} \text{ (2nd law)}^d}{\text{kcal (g-atom)}^{-1}}$	$\frac{\Delta S_{298}^{\circ} \text{ (2nd law)}^d}{\text{cal deg}^{-1} \text{ (g-atom)}^{-1}}$	$\frac{\Delta S_{298}^{\circ} \text{ (3rd law)}^c}{\text{cal deg}^{-1} \text{ (g-atom)}^{-1}}$
This study	111.873 ± 0.511^b	112.038 ± 6.197	34.459 ± 3.288	34.375
Edwards, Johnston, & Ditmars ⁷	111.796 ± 0.083^c	112.266 ± 0.754^e	34.661 ± 0.451^e	
This study with Edwards et al. ⁷	111.847 ± 0.411	111.337 ± 0.913	34.090 ± 0.506	
Blocher & Campbell ⁵	110.26 ± 0.58^c	$110.924 \pm 1.852^{e,f}$	34.831 ± 1.122^e	
Carpenter & Mair ⁶	110.71 ± 0.51^c	$112.492 \pm 4.259^{e,f}$	35.385 ± 2.456^e	
Strassmair & Stark ¹⁰	110.052 ± 0.400	111.763 ± 2.431^e	35.375 ± 1.461^e	

$$(a) \quad \Delta H_{298}^{\circ} = -RT \ln P \text{ (atm)} - T \left(\frac{G_T^{\circ} - H_{298}^{\circ}}{T} \right)_{\text{Ti(g)}}^c + T \left(\frac{G_T^{\circ} - H_{298}^{\circ}}{T} \right)_{\text{Ti(s,}\beta)}^c$$

Each data point gives a value for ΔH_{298}° . Data in these columns are the average values.

(b) All errors reported are standard deviations.

(c) From JANAF tables.³

(d) Derived from least squares analysis: $\ln p \text{ (atm)} = -\frac{\Delta H_T^{\circ}}{RT} + \frac{\Delta S_T^{\circ}}{R}$.

(e) Based on these authors' original data for P and T.

(f) Changes in emissivity of Ti do not significantly alter these values.

(g) Morrison⁸ and Kuz'min and Palatnik⁹ do not report their original P, T data. Morrison⁸ reports that his data fit $\log p \text{ (torr)} = 10.47 - \frac{24,600}{T}$, and Kuz'min and Palatnik⁹ data were fitted to $\log P \text{ (atm)} = 7.30 - \frac{24,200}{T}$.

DISCUSSION

In this research, the mass spectrometer results enabled one to conclude that the vapor species was predominantly Ti(g) . No observation of $\text{Ti}_2(\text{g})$ was made; an upper limit for $P[\text{Ti}_2(\text{g})]/P[\text{Ti(g)}]$ was set at 0.0028 from these measurements.

The vapor pressure measurements reported in this paper are the first measurements by the Knudsen method. These vapor pressure measurements are considered to be reliable within the cited error limits for $\Delta H_{298,\text{subl}}^\circ$ and $\Delta S_{298,\text{subl}}^\circ$ because (1) the second- and third-law $\Delta H_{298,\text{subl}}^\circ$ agree within experimental errors and (2) the second-law $\Delta S_{298,\text{subl}}^\circ$ agrees with the third-law value.

In the previous vapor pressure measurements performed by the Langmuir method, it was necessary to assume that the vaporization coefficient, α_v , was unity. Through orifice size variations in the present research, evidence was found which substantiates that α_v is unity.

Edwards, Johnston, and Ditmars⁷ measured the emissivity of $\text{Ti(s},\beta)$ as 0.43. The values of $\Delta H_{298,\text{subl}}^\circ$ and $\Delta S_{298,\text{subl}}^\circ$ from Edwards *et al.*⁷ and the present study agree well. This agreement supports the value for the emissivity of Edwards *et al.*⁷

The agreement of the present Knudsen measurements with the previous Langmuir measurements and the agreement of the second-law and third-law thermodynamic values support the assumption that the vapor pressures are not influenced by the W effusion cell. In the Langmuir measurements no container was used. If there had been extensive solid solution formation between the $\text{Ti(s},\beta)$ and W, the vapor pressures would have been too small.

The effect of oxygen in the residual gases in the vacuum is believed

to have had a minimal effect in these vapor pressure measurements. From the failure to observe TiO(g) or $\text{TiO}_2\text{(g)}$ with the mass spectrometer, the vapor pressure measurements were performed on a system for which the vapor species was predominantly Ti(g) . Another difficulty connected with the presence of oxygen is more difficult to assess; i.e., the effect of oxidation of the solid titanium. Oxygen could enter the effusion cell from the vacuum and produce a solid solution with the solid titanium. The metal was still bright and shiny in appearance after the vapor pressure measurements. It is believed that this effect was small because of no observed effects with aging and agreement with the previous Langmuir measurements in which the metal was exposed to the residual gases in the vacuum to a much greater extent.

From the analysis of the present vapor pressure measurements and the previous studies, $111.847 \pm 0.411 \text{ kcal (g-atom)}^{-1}$ is the recommended value for $\Delta H_{298, \text{subl}}^\circ$ of $\text{Ti(s,}\beta\text{)}$. This value results from the combined data of this study and the measurements of Edwards, Johnston, and Ditmars.⁷

The above recommended value for $\Delta H_{298, \text{subl}}^\circ$ of $\text{Ti(s,}\beta\text{)}$ together with the $\Delta H_{298, \text{f}}^\circ$ of $\text{Ti(s,}\beta\text{)}$ of $1.433 \text{ kcal mole}^{-1}$ ³ yields a value for $\Delta H_{298, \text{f}}^\circ$ of Ti(g) of $113.28 \pm 0.41 \text{ kcal mole}^{-1}$. At the present time JANAF³ is using a value of $\Delta H_{298, \text{f}}^\circ$ of Ti(g) of $113.0 \pm 1.0 \text{ kcal mole}^{-1}$. A recent report by Koch et al.¹⁹ reports a value for $\Delta H_{298, \text{subl}}^\circ$ of $\text{Ti(s,}\alpha\text{)}$ or $\Delta H_{298, \text{f}}^\circ$ of Ti(g) of $112.4 \pm 0.6 \text{ kcal mole}^{-1}$; this value is based on Langmuir vapor pressure measurements on liquid titanium. Hultgren, et al.⁴ has concluded that $\Delta H_{298, \text{subl}}^\circ$ of $\text{Ti(s,}\alpha\text{)}$ is $112.3 \pm 0.5 \text{ kcal/mole}$. All of the above values agree within the reported experimental uncertainties.

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CAPTION FOR FIGURE

Figure 1 - Vapor pressure data for Ti(s,β) is presented as $\log_{10} P$ (atm) vs. $10^4/T^\circ\text{K}$. The lines which are drawn are derived by the third-law method from the original data of P and T from each group of investigators. If the value of the emissivity as measured by Edwards et al.⁷ is used on the data of Blocher and Campbell⁵ (B-C) and Carpenter and Mair⁶ (C-M), their data would be translated to the left in the figure to give better agreement. Strassmair and Stark¹⁰ data are shown by S-S. The data points of Edwards et al.⁷ are given by ●. The data of the present study are: ○, orifice A; △, orifice B; □, orifice C. The data of this study agree well with the data of Edwards et al.⁷; the line through these data is based on third-law values of $\Delta H_{298, \text{subl}}^\circ$ of 111.847 kcal (g-atom)⁻¹ and $\Delta S_{298, \text{subl}}^\circ$ of 34.375 cal (deg g-atom)⁻¹. These values and values of $\frac{G_T^\circ - H_{298}^\circ}{T}$ permit one to calculate the vapor pressure of Ti(s,β).