Effusion VI. Velocity Distributions of Gaseous CsCl from
Near-Ideal and Right-Circular Cylindrical Orifices¹

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(Received

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¹Based in part on a thesis by K. C. Wang submitted in partial fulfillment of the requirements for the Ph.D. degree, Illinois Institute of Technology, Chicago, Illinois, 1966. Parts of this paper were presented at the 156th American Chemical Society national meeting, Atlantic City, New Jersey, September 1968.

Abstract:

Velocity distributions have been measured for CsCl(g) effusing from double-oven effusion cells equipped with a near-ideal and non-ideal, 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, data show no dependence on Knudsen number (ratio of mean free path to orifice diameter) or effusion angle; non-ideal 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

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previously published angular number distributions may be explained by introducing some specular reflection on the orifice wall for the non-ideal orifices. Both sets of data were combined to yield angular momentum distributions.

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INTRODUCTION

In previous papers in the series,²⁻⁶ angular number distribution

²K. C. Wang and P. G. Wahlbeck, J. Chem. Phys. 47, 4799 (1967), Paper I.

³P. G. Wahlbeck and T. E. Phipps, ibid. 49, 1603 (1968), Paper II.

⁴J. Q. Adams, T. E. Phipps, and P. G. Wahlbeck, ibid. 49, 1609 (1968), Paper III.

⁵K. C. Wang and P. G. Wahlbeck, ibid. 49, 1617 (1968), Paper IV.

⁶J. Q. Adams, T. E. Phipps, and P. G. Wahlbeck, ibid. 51, 920 (1969), Paper V.

measurements have been reported for molecules effusing from a near-ideal orifice², from right-circular cylindrical orifices³⁻⁵, and from a conical orifice.⁶ 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 Clausing⁷⁻¹⁰ theory for non-ideal orifices (cylindrical and

⁷P. Clausing, Koninkl. Ned. Akad. Wetenschap. Proc. 35, 1023 (1926).

⁸P. Clausing, Physica 9, 65 (1929).

⁹P. Clausing, Z. Physik 66, 471 (1930).

¹⁰P. Clausing, Ann. Physik Ser. 5, 12, 961 (1932).

conical) has not been observed to be correct.

3) A fluctuation phenomenon was observed for CsCl(g) effusing from Cu and Ni cylindrical orifices^{4,5} and a Cu conical orifice⁶ (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.⁵

5) An upper pressure limit was found for the molecular flow region separating it from the transition region.^{2,5}

6) With increasing pressure in the transition region, the probability of effusion in the forward direction increases with the ideal orifice² and decreases with a long non-ideal orifice.^{3,4,5,6,11}

¹¹This conclusion is valid for a long hyperbolic orifice; see E. W. Clower, Ph.D. thesis, University of Illinois, Urbana, Illinois, 1954.

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 Maxwell¹² concluded

¹²See E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Company, New York, 1938.

that the velocity distribution of molecules in a gas should be

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

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 equation (1) must be multiplied by C . Velocity selectors are designed to operate at constant resolution; $R = \delta C/2C$. Thus, the distribution that exits from a velocity selector has the same form as given by equation (1) but must be multiplied by C^2 . For the "beam" molecules exiting from a velocity selector, the most probable velocity, C_{MP} , is

$$C_{MP} = \sqrt{\frac{4kT}{m}} \quad (2)$$

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

$$\bar{C} = \frac{4}{3} \sqrt{\frac{8kT}{\pi m}} \quad (3)$$

Velocity distributions have been measured previously.¹³⁻²³ These

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- ¹³J. Eldridge, Phys. Rev. 30, 931 (1927).
 - ¹⁴B. Lammert, Z. Physik 56, 244 (1929).
 - ¹⁵I. F. Zartman, Phys. Rev. 37, 383 (1931).
 - ¹⁶C. C. Ko, J. Franklin Inst. 217, 173 (1934).
 - ¹⁷V. W. Cohen and A. Ellett, Phys. Rev. 52, 502 (1937).
 - ¹⁸I. Estermann, O. C. Simpson, and O. Stern, Phys. Rev. 71, 238 (1947).
 - ¹⁹I. Kofsky and H. Levinstein, Phys. Rev. 74, 500 (1948).
 - ²⁰A. Bennett, Jr., Phys. Rev. 95, 608 (1954).
 - ²¹R. C. Miller and P. Kusch, Phys. Rev. 99, 1314 (1955).
 - ²²J. E. Scott, Jr., H. S. Morton, Jr., J. A. Phipps, and J. F. Moonan, Rarefied Gas Dynamics Symposium Supp. 3, Vol. II, 331 (1966).
 - ²³P. B. Scott, P. H. Bauer, H. Y. Wachman, and L. Trilling, ibid. Supp. 4, Vol. II, 1353 (1967).
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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 non-ideal orifices and high gas pressures (transition region), have been noted.²⁰⁻²³ 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.¹⁸ and by Scott et al.²²

In this study velocity distributions of molecules effusing from a

near-ideal orifice and right-circular cylindrical orifices have been measured. These distributions 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 Kusch;²¹ 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 Bernstein²⁴ constructed a velocity selector consisting

²⁴H. U. Hostettler and R. B. Bernstein, Rev. Sci. Instr. 31, 872 (1960).

of several thin disks with straight slots radially cut into the disks.

The velocity selector may be viewed as approximating sections of the Miller and Kusch²¹ velocity selector. Trujillo et al.²⁵ have constructed

²⁵S. M. Trujillo, P. K. Rol, and E. W. Rothe, Rev. Sci. Instr. 33, 841 (1962).

a similar velocity selector.

A better approximation to the helical slot velocity selector of Miller and Kusch²¹ 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.²² 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 non-ideal orifices. In addition the velocity distribution data and the angular number distributions already reported²⁻⁵ yielded angular momentum distributions; the angular momentum distributions are of interest to those using the torsion effusion method and other momentum methods.²⁶

²⁶R. D. Freeman, in "The Characterization of High Temperature Vapors," Ed. J. L. Margrave, John Wiley and Sons, Inc., New York, 1967, P. 152.

EXPERIMENTAL

Apparatus

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

The portion of the apparatus concerned with the rotation of the effusion cell has been discussed previously.² 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 previously;² 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 orifice² and two right-circular cylindrical orifices.⁵ 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.²

The design and principles of operation of the surface ionization detectors have been discussed previously.² A Re filament was used in these experiments. The detector indicated in Figure 1 as being nearest the effusion cell (right) was used for the angular number distribution studies previously reported. The detector farthest from the effusion

Table I. Characteristics of the Orifices

Property	Near-Ideal	Short	Long
Material	Ni body with orifice in Pt	Cu OFHC	Ni Grade A
L, length, mm	0.013	0.196	0.440
d, diameter, mm	0.50	0.42	0.34
L/d	0.026	0.466	1.294

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 Figure 1, was amplified with a vibrating reed electrometer; the conversion of ion currents to molecular intensities has been discussed previously.²

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 Figure 1.

The synchronous motor and variable frequency power supply used to drive the velocity selector were the same as used by Hostettler and Bernstein.²⁴

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

Procedure

Evacuation and effusion cell heating procedures have been discussed previously.²

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 recorder during the deceleration of the velocity selector. For earlier measurements with both non-ideal orifices, these two signals were

simultaneously recorded with a two-pen recorder. An example of an experimental distribution is given in Figure 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 $\phi_2 = 0.2443_5$ rad. Thus by equation (5), the two transmitted velocities were such that C_2/C_1 was 0.6818_2 (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 distributions¹³⁻²³ 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.¹⁸, Miller and Kusch,²¹ and Scott et al.²³ On this basis and on the basis of the agreement of angular number distributions from this near-ideal orifice² with the "cosine law of effusion," the velocity distributions were expected to be Maxwellian.

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 equation (1). The fitting was accomplished by means of a non-linear least squares program written by Struble.²⁷ An example of this fitting is shown in Figure 3.

²⁷G. Struble, "Non-linear Least Squares Curve Fitting Program," IBM 1620 General Program Library, 6.0.134.

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 .²⁸ For each series with the near-ideal orifice, the values of A_T were

²⁸This conclusion has been justified through the analyses of data as a function of detector position.

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}^{theo} , and $\bar{C}^{theo}$; (2) dependence on effusion angle θ ; and (3) dependence on the state of $CsCl(g)$ (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 $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ and $C_{\text{MP}}^{\text{exp}} / C_{\text{MP}}^{\text{theo}}$ derived from the velocity distribution data at $\theta = 0$. The average of $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ values and of $C_{\text{MP}}^{\text{exp}} / C_{\text{MP}}^{\text{theo}}$ 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 Figure 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 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 Figure 5 the effect of the pressure of CsCl(g) on the velocity distribution is examined; $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ at $\theta = 0$ is plotted vs. $\log Z$, where Z is the number of wall collisions $\text{cm}^{-2} \text{ sec}^{-1}$. From these data, increasing P_{CsCl} had no effect on the velocity distribution. In addition ΔT , $T(\text{F}) - T(\text{B})$, for each run is indicated; this shows that $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ is not dependent on ΔT .

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

Table II. Conditions of CsCl(g); Near-Ideal Orifice Runs

Run	T(F)°K	T(B)°K	ΔT	$Z \times 10^{-18}{}^a$ (molecules cm ⁻² sec ⁻¹)	P (mmHg) ^b	K ^c	$\bar{C}^{\text{exp}}/\bar{C}^{\text{theo}}{}^d$	$C_{\text{MP}}^{\text{exp}}/C_{\text{MP}}^{\text{theo}}{}^d$
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

$${}^a Z = p (2\pi mk T(F))^{-1/2}$$

$${}^b \text{For } T(B) < 915^\circ\text{K}, \log_{10} P_{\text{mm Hg}} = -(9970/T(B)) + 9.942$$

$${}^c K = \frac{\lambda_{\text{Maxwell}}}{d}, \lambda_{\text{Maxwell}} = kT/\sqrt{2\pi\sigma^2} p, \text{ where } \sigma = 7.015 \text{ \AA} \text{ from the average of atomic and ionic diameters taken from N. A. Lange, Handbook of Chemistry (Handbook Publishers, Inc. New York, 1961), 10th ed.}$$

$${}^d \text{Data for } \theta = 0^\circ$$

Table III. Velocity Distribution Data for the Three Orifices

Orifice	L/d	Runs	$\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}^a$	$C_{\text{MP}}^{\text{exp}} / C_{\text{MP}}^{\text{theo}}^a$
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

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

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 $\bar{C}^{\text{exp}}/\bar{C}^{\text{theo}}$ and $C_{\text{MP}}^{\text{exp}}/C_{\text{MP}}^{\text{theo}}$ 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 Figure 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 $\bar{C}^{\text{exp}}/\bar{C}^{\text{theo}}$ and $C_{\text{MP}}^{\text{exp}}/C_{\text{MP}}^{\text{theo}}$ 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 that $\bar{C}^{\text{exp}}/\bar{C}^{\text{theo}}$ and $C_{\text{MP}}^{\text{exp}}/C_{\text{MP}}^{\text{theo}}$ 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:

$$\bar{C}^{\text{exp}}/\bar{C}^{\text{theo}} = (A + B P_{\text{CsCl}} + C P_{\text{CsCl}}^2) (1 + D \Delta T) (1 + E \theta), \quad (7)$$

where A, B, C, D, and E are fitted parameters obtained from the non-linear least-squares program.²⁷ Table VI summarizes the values of the parameters determined for each cylindrical orifice.

A graphical representation of the fitting of the experimental data by equation (7) may be seen for the long orifice in Figure 8 and for the

Table IV. Conditions of CsCl(g); Short Orifice Runs

Run	T(F) °K	T(B) °K	ΔT	$Z \times 10^{-18}{}^a$ (molecules $\text{cm}^{-2}\text{sec}^{-1}$)	$P_{(\text{mmHg})}{}^b$	k^c	$\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}{}^d$	$C_{\text{MP}}^{\text{exp}} / C_{\text{MP}}^{\text{theo}}{}^d$
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

^aSee note (a) of Table II.^bSee note (b) of Table II.^cSee note (c) of Table II.^dSee note (d) of Table II.

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 _(mmHg) ^b	K ^c	$\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}{}^d$	$C_{\text{MP}}^{\text{exp}} / C_{\text{MP}}^{\text{theo}}{}^d$
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

Table V. Conditions of CsCl(g); Long Orifice Runs (Continued)

Run	T(F) _{°K}	T(B) _{°K}	ΔT	$Z \times 10^{-18}{}^a$ (molecules cm ⁻² sec ⁻¹)	P (mmHg) ^b	K ^c	$\bar{C}^{\text{exp}}/\bar{C}^{\text{theo}}{}^d$	$C_{\text{MP}}^{\text{exp}}/C_{\text{MP}}^{\text{theo}}{}^d$
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

Footnotes for Table V.

^aSee note (a) of Table II.

^bSee note (b) of Table II.

^cSee note (c) of Table II.

^dSee note (d) of Table II.

Table VI. Values of Parameters for Equation (7)

	<u>Long Orifice Data</u>		<u>Short Orifice Data</u>	
	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

short orifice in Figure 9. These two figures show that $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ increases with P_{CsCl} (or Z) and decreases with θ for both long and short orifices. The dependence of $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ and $C_{\text{MP}}^{\text{exp}} / C_{\text{MP}}^{\text{theo}}$ 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 V. Even with the scatter in the experimental data, these dependences upon Z and θ are significant.

The dependence of $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ upon ΔT was believed to be significant during preliminary analyses of the data. The analyses of the data using equation (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 Figures 4, 5, and 6 and Tables II and III. The experimental velocity distributions, within experimental error, show no dependence on K , Knudsen number (or Z or P_{CsCl}); on θ , 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,² 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.

Non-Ideal Cylindrical Orifices

The experimental velocity distributions of molecules effusing from both the short and long non-ideal cylindrical orifices showed deviations from the Maxwellian velocity distribution; this may be seen from data presented in Tables III, IV and V and Figures 7, 8, and 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^{18,22} occurring during the effusion process can cause deviations from a Maxwellian theoretical velocity distribution. However, deviations seen at low pressures with the non-ideal 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 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,²⁹ will

²⁹R. T. Grimley and John LaRue, Rarefied Gas Dynamics Symposium, Supp. 5 (1969) (to appear).

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 CsCl(g) would have to decrease by a factor of 10^{+10} in order to raise $P_{\text{Cs}}/P_{\text{CsCl}}$ to ca. 1. Thus, the probability of Cs(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 CsCl(g) on the orifice wall of the effusion cell.

If the orifice wall and near-by effusion-cell wall were at a temperature lower than $T(\text{F})$ (the heater and thermocouple locations would not allow a temperature higher than $T(\text{F})$), 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 $T(\text{F})$ 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 non-isothermal wall in the front oven.

With the removal of these possibilities of apparatus malfunction, gas-phase collisions, thermal dissociation, surface ionization, and non-isothermal conditions, it is concluded that the deviations observed were caused by effusing CsCl(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 CsCl(g) effusing from these same cylindrical orifices,⁵ 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.^{30,31} Specular

³⁰R. M. Logan and R. E. Stickney, J. Chem. Phys. 44, 195 (1966).

³¹R. M. Logan, J. C. Keck, and R. E. Stickney, Rarefied Gas Dynamics Symposium, Supp. 4, Vol. I, 49 (1967)

reflection has been observed with Ar and N₂ molecular beams impinging on polycrystalline Ni by Fisher, Hagen, and Wilmoth.³²

³²S. S. Fisher, O. F. Hagen, and R. G. Wilmoth, J. Chem. Phys. 49, 1562 (1968).

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.⁵

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 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.

Previously⁵ 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 Figure 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, $P(\theta)_{\text{exp}} \bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$, 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 0.50.³³ 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 non-ideal 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 phenomena occurs.

ACKNOWLEDGMENTS

The authors express their gratitude to the U.S. Atomic Energy Commission for financial support through contract AT (11-1)-1029. For machine shop work, we wish to thank Mr. Jack Lawson of the IITRI machine shop and Mr. Harlan Hertrich of the Chemistry Department machine shop.

FIGURE CAPTIONS

- 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.² 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 0.0813 cm thick. The overall length of the selector was 11.20 cm. The "helix" angle ϕ was 0.1666 rad.
- Fig. 2 Laboratory Velocity Distribution Data. The ordinate is relative I^+ (signal from vibrating reed electrometer). The abscissa is velocity (C_1 ; signal from angular velocity tachometer); 1 cm = 3389.7 cm/sec. The signal to noise ratio of these data are of intermediate quality.
- Fig. 3 Fitting of Two Maxwellian Velocity Distributions to Laboratory Data. Data $\bigcirc$ are from Run 13 (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 $\square$, ---, are from Run 13 (near-ideal orifice), $\theta = 0$; see Fig. 3. Maxwellian distribution is represented by $\bigcirc$, ———. The agreement of these data with Maxwellian is of intermediate quality. Abscissa: 1 unit $C = 3389.7$ cm/sec.
- Fig. 5 Near-ideal Orifice Data. Upper plot: $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ vs. $\log Z$; lower plot: ΔT vs. $\log Z$. These values of $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ do not show any dependence on $\log Z$ or on ΔT .

Fig. 6 Near-ideal Orifice Data. $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ 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 $\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}}$ on θ .

Fig. 7 Velocity Distributions for the Near-Ideal Orifice and Long Orifice for similar low pressure states of CsCl(g).
 I_{rel} vs. C_{red} ($C_{\text{red}} = \frac{C}{C_{\text{MP}}^{\text{theo}}}$).

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.

Fig. 8 Long Orifice Velocity Distribution Data. Coordinates are $\bar{C}_R (\bar{C}^{\text{exp}} / \bar{C}^{\text{theo}})$, Z and θ . The black balls are calculated points from the fitting of experimental data to equation (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^{18} moles/sec.

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} moles sec^{-1} .

Fig. 10 Angular momentum distribution data for the long orifice.

$P_m(\theta) = P(\theta) \cdot \bar{C}/\bar{C}^{\text{theo}}$, where $P(\theta)$ is the probability density function derived from the angular number distribution data.

————— $P(\theta)_{\text{Clausing}} \cdot \frac{\bar{C}^{\text{theo}}}{\bar{C}^{\text{theo}}}$; theoretical Clausing angular number distribution with a Maxwellian velocity distribution.

----- $P(\theta)_{\text{exp}} \cdot \frac{\bar{C}^{\text{theo}}}{\bar{C}^{\text{theo}}}$; experimental angular number distribution, Run K69 (see Ref. 5), $K = 2.53$, with a Maxwellian velocity distribution.

————— $P(\theta)_{\text{exp}} \cdot \frac{\bar{C}^{\text{exp}}}{\bar{C}^{\text{theo}}}$; same experimental angular number distribution with a calculated $\bar{C}^{\text{exp}}/\bar{C}^{\text{theo}}$ from equation (7).

There is a larger momentum component in the forward direction than indicated by the theoretical distributions.

Fig. I APPARATUS

I_{rel}^+

→ | ← 1 Cm

C

Fig. 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 10