The average value from Table I was corrected for 0.02 mole % CF_4 using −39.3 kcal. per mole as the energy of reaction of CF_4 and hydrogen. The corrected figure for $-\Delta E^0r/M$ is 2793.0 cal. per gram. Using atomic weights of 14.0067 for N and 18.9984 for F, the molar energy of reaction is $\Delta E^0r = -198.31$ kcal. per mole. The reaction to which this refers is:

$$NF_3(g) + \tfrac{3}{2} H_2(g) \rightarrow \tfrac{1}{2} N_2(g) + 3HF(1 \text{ in } 123\ H_2O)$$

Correcting to constant pressure conditions: $\Delta H^0r_{298} = -199.49 \pm 0.22$ kcal. per mole. The uncertainty is twice the over-all standard deviation.

Armstrong, Marantz, and Coyle (*1*) quoted −202.1 kcal. per mole based on NF_3 dosage and −208.4 kcal. per mole based on HF recovery, with the HF adjusted to infinite dilution. On the same basis for HF, the present work gives −208.40 kcal. per mole, in exact agreement with the value based on HF recovery. It would appear that the NF_3 used by Armstrong and coworkers was less pure than they estimated.

Ludwig and Cooper (*5*) measured the heat of reaction of boron and nitrogen trifluoride and derived $\Delta Hf_{298}(NF_3, g) = -30.4 \pm 1.2$ kcal. per mole. Employing this value and the present work yields $\Delta Hf_{298}(HF, 1 \text{ in } 123\ H_2O) = -76.63$ kcal. per mole. This is 0.94 kcal. per mole more negative than the value listed in Circular 500 (*7*). The heat of formation of ideal gaseous HF is also probably more negative than the value selected for Circular 500 (*2*). There is obviously a need for revision of the thermochemical values for gaseous HF and its aqueous solutions.

LITERATURE CITED

(1) Armstrong, G.T., Marantz, S., Coyle, C.F., *J. Am. Chem. Soc.* **81**, 3798 (1959).
(2) Feder, H.M., Hubbard, W.N., Wise, S.S., Margrave, J.L., *J. Phys. Chem.* **67**, 1148 (1963).
(3) Hubbard, W.N., Katz, C., Waddington, G., *Ibid.*, **58**, 142 (1954).
(4) Jarry, R.L., Miller, H.C., *Ibid.*, **60**, 1412 (1956).
(5) Ludwig, J.R., Cooper, W.J., J. Chem. Eng. Data **8**, 76 (1963).
(6) Nuttall, R.L., Wise, S., Hubbard, W.N., *Rev. Sci. Instr.* **32**, 1402 (1961).
(7) Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., Jaffe, I., *Natl. Bur. Std., (U. S.), Circ.* **500**, 1952.
(8) Ruff, O., Wallauer, H., *Z. anorg. allgem. Chem.* **196**, 421 (1931).

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Vaporization and Sublimation of $SrCl_2$

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The sublimation and vaporization rates of $SrCl_2$ have been determined by means of the Langmuir and Knudsen techniques, respectively. The third-law heat of sublimation at 298° K. is 78.6 ± 1.0 kcal. mole^{-1}.

VAPOR PRESSURES and sublimation pressures for several alkaline earth dihalides are now available, but no extended Langmuir and Knudsen study or mass spectrometric characterization of the vapor over condensed $SrCl_2$ has been published. Neither has there been a careful consideration of the evaporation coefficient for any alkaline earth dihalide both above and below the melting point. A comparison of the torque-Knudsen, Langmuir, and mass spectrometric results for CaF_2 (*2, 3, 10, 13*) and BaF_2 (*1, 7, 8*) suggests that α_L, the Langmuir evaporation coefficient, may be 0.1 to 0.3 for CaF_2 (g) or BaF_2 (g) subliming from the solid fluorides. Burns (*5*) recently observed a discontinuous change in α_L for the vapor species over condensed Al_2O_3 at the melting point.

This paper reports Langmuir and Knudsen weight loss studies, a mass-spectrometric characterization of the vapor, and calculation of α_L for $SrCl_2$.

EXPERIMENTAL

The Langmuir studies were made with a sample of single-crystal $SrCl_2$ obtained from Semi-elements, Inc. The crystal was suspended from a tungsten support wire inside a quartz envelope mounted below one pan of an Ainsworth RVA-AU-2 semi-micro recording balance. A Kanthal wire-wound resistance furnace controlled by a West Model JP temperature controller was used to heat the sample. The rate of weight loss was automatically recorded while temperature measurements were made with a Pt–Pt 10% Rh

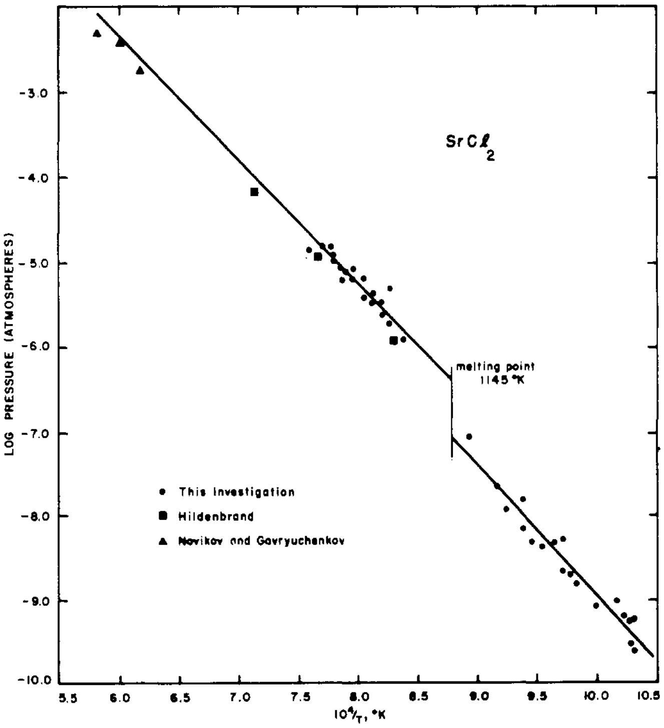

Figure 1. Vapor pressure of $SrCl_2$ by various investigators

Table I. Langmuir Sublimation Data for $SrCl_2$

T, °K.	$\Delta w \times 10^4$, Grams	Δt, Sec.	$-\log P$, Atm.	$\Delta\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$, Cal. Mole^{-1} Deg.$^{-1}$	ΔH_{298}° (sub), Kcal Mole^{-1}
985	3.1	5,040	9.001	40.27	80.24
1037	18.2	5,040	8.222	40.00	80.49
1039	6.1	1,920	8.227	40.00	80.68
1067	16.6	1,800	7.807	39.85	80.63
1119	19.5	360	7.029	39.58	80.28
969	1.8	5,520	9.281	40.33	80.23
974	0.5	1,440	9.252	40.21	80.40
971	1.3	4,200	9.302	40.32	81.32
970	1.3	6,720	9.509	40.32	81.32
968	1.2	8,040	9.622	40.34	81.67
999	4.7	8,280	9.033	40.21	81.46
1015	7.4	7,680	8.799	40.13	81.60
1018	8.9	8,760	8.697	40.10	81.34
1027	16.6	12,960	8.674	40.06	81.90
1050	8.3	3,000	8.336	39.94	81.98
1055	10.3	3,360	8.291	39.92	82.14
1062	19.8	4,800	8.158	39.88	82.00
1081	24.2	3,240	7.896	39.78	81.98
1090	31.8	2,400	7.644	39.73	81.43
					Av. = 81.2 ± 0.70

Area $SrCl_2$ crystal = 3.47 cm.^{2}

$\log P$ (atm.) = $-(1.56 \pm 0.077) \times 10^4 T + (6.70 \pm 0.14)$

Table II. Knudsen Vaporization Data for $SrCl_2$

T, °K.	$\Delta w \times 10^4$, Grams	Δt, Sec.	$-\log P$, Atm.	$\Delta\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$, Cal. Mole^{-1} Deg.$^{-1}$	ΔH_{298}° (vap), Kcal. Mole^{-1}
1219[a]	4.7	6,120	5.499	39.06	78.28
1212	2.4	2,400	5.385	39.10	77.25
1228	7.8	7,680	5.376	39.01	78.11
1242	7.4	5,400	5.243	38.94	78.16
1252	8.8	4,200	5.057	38.89	77.66
1278	15.2	5,160	4.904	38.75	78.20
1272	14.9	6,120	4.988	38.79	78.37
1285	15.0	4,920	4.888	38.71	78.49
1264	5.4	3,840	5.228	38.83	79.32
1307	13.0	3,720	4.826	38.60	79.31
1195[b]	13.7	6,480	5.879	39.19	78.98
1209	11.5	3,960	5.711	39.11	78.88
1220	12.1	3,000	5.575	39.06	78.78
1227	22.1	4,560	5.510	39.02	78.81
1242	10.0	1,800	5.370	38.94	78.88
1254	9.9	10,800	5.225	38.88	78.74
1262	18.7	13,920	5.144	38.84	78.72
1266	14.7	8,040	5.084	38.81	78.58
1273	14.1	2,280	5.036	38.78	78.70
					Av. = 78.6 ± 0.4

$\log P$ (atm.) = $-(1.439 \pm 0.113) \times 10^4/T + (6.28 \pm 0.09)$. [a] For lid No. 1 (first 10 points), orifice diameter = 0.788 mm., Clausing factor $W_o = 0.3105$. [b] For lid No. 2 (last 9 points), orifice diameter = 1.235 mm., Clausing factor $W_o = 0.3581$.

thermocouple suspended near the sample. The thermocouple was calibrated against a standard thermocouple from the National Bureau of Standards. The pressure inside the system was monitored by means of an ionization gage and was maintained below 2×10^{-6} torr during the runs while the temperature remained constant to within ±3° K.

For measurements above the melting point of $SrCl_2$, Knudsen cells were machined from high-density, spectroscopic-grade graphite rods. Clausing factors for the cell lids were calculated using the results of Iczkowski, Margrave, and Robinson (*11*). Experiments in which the vapor over $SrCl_2$ was effused from Vycor Knudsen cells into a Bendix time-of-flight mass spectrometer yielded only $SrCl^+$ ions.

The various data obtained from the Langmuir and Knudsen measurements (968 to 1307° K.) were fitted to the equation $\log P = B - A/T$ by the method of least-squares using a digital computer.

RESULTS AND DISCUSSION

The mass spectrometric observation of only $SrCl^+$ ions is typical for alkaline earth dihalides which have previously been shown to undergo dissociative ionization on electron impact (*2, 3, 7, 10*). Thus, in all calculations from the Knudsen and Langmuir weight loss data, $SrCl_2$(g) is assumed as the major vapor species. The results and calculated heats of sublimation and vaporization, based on the free energy and heat content functions of Brewer and coworkers (*4*), and of Dworkin and Bredig (*6*), are presented in Tables I and II. The data points are shown in Figure 1, along with some recent direct boiling point measurements (*12*) and unpublished torque-Knudsen work (*9*) with the least-squares derived equations shown as solid lines. The vapor pressure values determined in this work agree with those of Van Westenburg (*14*) within the limits commonly observed for this type of measurement.

The second-law heats for the Langmuir and Knudsen experiments are identical, within experimental error, when corrected to 298° K. (77.6 ± 3.5 kcal. mole^{-1} and 78.4 ± 5.2 kcal. mole^{-1}, respectively). In contrast, the third-law heats, which depend directly on the absolute pressures, show that the hypothetical Langmuir sublimation at 298° K. requires 2.6 ± 1.0 kcal. mole^{-1} more energy than predicted by the Knudsen data. This suggests $\alpha_L = 0.3 \pm 0.2$ for $SrCl_2$(g) subliming from $SrCl_2$(s). The uncertainties in the second-law heats are such that this activation energy is within these limits.

Similar discrepancies between Langmuir and Knudsen studies of CaF_2 (*2, 3, 7, 10, 13*) and BaF_2 (*1, 7, 8*) have been noted and support the idea that monomeric MX_2(g) species escape from single crystal surfaces into vacuum at a rate slower than predicted by thermodynamic data—i.e.—$\alpha_L < 1$. Qualitative calculations for CaF_2 and BaF_2 show the α's to fall in the range 0.1 to 0.5, in agreement with the data presented here.

From the dimensions of the orifices used in the various Knudsen measurements on alkaline earth dihalides, one estimates α_c, the condensation coefficient for MCl_2(g) on MCl_2(l), is in the range 0.8 to 1.0.

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LITERATURE CITED

(1) Bautista, R.G., Margrave, J.L., *J. Phys. Chem.* **69**, 1770 (1965).

(2) Berkowitz, J., Marquart, J.R., *J. Chem. Phys.* **37**, 1853 (1962).

(3) Blue, G.D., Green, J.W., Bautista, R.G., Margrave, J.L., *J. Phys. Chem.* **67**, 877 (1963).

(4) Brewer, L., Somayajulu, G., Brackett, E., *Chem. Rev.* **63**, 111 (1963).

(5) Burns, R.P., Jason, A.J., Inghram, M.G., *J. Chem. Phys.* **40**, 1661 (1964).

(6) Dworkin, A.S., Bredig, M.A., *J. Phys. Chem.* **67**, 697 (1963).

(7) Green, J.W., Blue, G.D., Ehlert, T.C., Margrave, J.L., *J. Chem. Phys.* **41**, 2245 (1964).

(8) Hart, P.E., Searcy, A.W., University of California Radiation Laboratory, U.C.R.L.-**11129**, January 16, 1964.

(9) Hildenbrand, D.L., Aeronutronics, Newport Beach, Calif., private communication, 1964.

(10) Hildenbrand, D.L., *J. Chem. Phys.* **40**, 3438 (1964).

(11) Iczkowski, R.P., Margrave, J.L., Robinson, S.M., *J. Phys. Chem.* **67**, 229 (1963).

(12) Novikov, G.I., Gavryuchenkov, F.G., *Zh. Neorgan. Khim.* **9**, 475 (1963).

(13) Schultz, D.A., Searcy, A.W., *J. Phys. Chem.* **67**, 103 (1963).

(14) Van Westenberg, J.A., *Dissertation Abstr.* **25**, 1129 (1964).

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