

Vapor Pressures of Yttrium and Rare Earth Chlorides Above Their Melting Points

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The Knudsen molecular effusion method was used to determine the vapor pressures of the following chlorides above their melting points: YCl_3 , LaCl_3 , CeCl_3 , PrCl_3 , NdCl_3 , SmCl_2 , EuCl_3 , GdCl_3 , TbCl_3 , DyCl_3 , HoCl_3 , ErCl_3 , TmCl_3 , YbCl_3 , and LuCl_3 . Heats of vaporization were calculated for each salt from linear plots of $\log_{10} P$ vs. $1/T$, using the Clausius-Clapeyron relationship.

INCREASED industrial application of the rare earth halides has stimulated interest in these materials. Despite the long standing use of rare earth halides for the preparation of the rare earth metals and in other applications, there is a distinct dearth of data on some of the properties of these compounds. This investigation was initiated to determine experimentally the vapor pressures of some anhydrous rare earth chlorides.

The chlorides were prepared in anhydrous form employing a method similar to the one reported by Reed *et al.* (4). The salts were made from high purity rare earth oxides (99.9%) and were relatively free of oxychlorides. Nine of the 15 salts studied were examined with X-ray diffraction powder techniques. Trichlorides of yttrium and the rare earths appeared to be thermally stable within the temperature ranges studied except for SmCl_3 . In the case of samarium, chlorine was lost under reduced pressure at elevated temperature in two separate experiments, and an approximate 1:2 stoichiometry was reached. For this salt (SmCl_2), the vapor pressures were measured independently after the decomposition of SmCl_3 . Ytterbium trichloride seemed to behave and not decompose in the temperature range examined, as evidenced by melting point determinations and the data presented in Table II. The data shown for EuCl_3 might indicate a tendency toward decomposition, although an extrapolated value for the 2-mm. Hg vapor pressure temperature agrees closely with an earlier estimate (1).

Because of increased data reliability, the vapor pressures reported were measured above the melting point of each salt. Also, in most instances this is the region of practical importance. Harrison (2) has reported the vapor pressures of a limited number of rare earth halides measured in a region near their melting points and below.

EXPERIMENTAL

The Knudsen molecular effusion method (6, 8) was employed to determine the vapor pressures. Briefly, the method consists of determining the effusion rate through a small orifice from a vaporization cell at a constant temperature in a vacuum. The weight of effused vapor is converted to pressure using an expression based upon the kinetic theory of gases. The mass G (grams) lost per second per square centimeter through the knife-edge orifice is related

to pressure P (mm. of Hg) by the equation, $P = 17.14G \cdot (T/M)^{1/2}$, provided the molecular mean free path exceeds the orifice dimension. The orifice diameter (2.5 mm.) was measured with a metallurgical microscope.

All experimental data were collected using the effusion apparatus shown in Figure 1. A quantity of from 15 to 50 grams of chloride was placed in a preweighed, 1-inch internal diameter, 316 S.S. crucible (L). The crucible was placed in the stainless steel effusion cell (K) and the 310 S.S. orifice plate (J) inserted into a recessed channel in the cell. On top of this plate stood a condensing sleeve (I). This assembly was lowered into the 310 S.S. bomb (G) and the bomb cover plate (C) and pressure plate (B) were affixed. The crucible temperature was sensed with a calibrated Chromel-Alumel thermocouple inside the well (H) and recorded on a Hoskins Thermo-Electric Pyrometer, to an accuracy of $\pm 2^\circ \text{C}$. The bomb assembly was heated in an electric glow-bar furnace, the temperature being controlled with a Leeds and Northrup recording potentiometer. The vacuum system consisted of a three-stage oil diffusion pump backed by a Stokes-Microvac mechanical pump. The reduced pressure was measured with both an Asco vacuum gage and a Flosdorf-type McLeod gage. During an experimental run the pressure was maintained between 10^{-3} and 10^{-4} mm. of Hg.

The evacuated bomb was filled with dry argon to 2 atm. gage pressure and placed in the furnace. When the crucible attained the desired equilibrium temperature, the system was evacuated for a measured period of time (usually 1 hour), at the end of which the bomb was again pressurized with argon and removed from the furnace. When the apparatus had sufficiently cooled, the crucible was removed and the weight of vapor effused was determined. The ratio of the orifice area to the molten salt surface was approximately 1:100.

Between each pressure measurement the effusion apparatus was dismantled and the cell body (K), orifice plate (J), and condensing sleeve (I) were cleansed with water and dried. The diameter of the knife edge orifice was measured microscopically. This value did not vary over ± 0.06 mm. in more than 60 hours of service. This indicated only slight attack by a current of hot chloride vapors on 310 stainless steel. At the completion of a series of pressure determinations for an individual salt, the crucible (L) was soaked in water to remove remaining chloride.

Table I. Vapor Pressure Empirical Data

Compound	Pressure, mm. Hg $\times 10^2$	Temp., $^{\circ}$ C.	$1/T$ $^{\circ}$ K. $^{-1} \times 10^3$
YCl ₃	6.11	700	1.028
	11.37	750	0.976
	55.70	850	0.890
	210.00	985	0.795
	29.10	810	0.922
	102.10	900	0.852
LaCl ₃	16.90	900	0.852
	44.62	940	0.824
	153.91	980	0.797
CeCl ₃	7.89	870	0.874
	11.00	900	0.852
	18.81	925	0.836
	25.60	950	0.817
PrCl ₃	5.11	835	0.903
	12.71	900	0.852
	24.80	945	0.821
	72.61	1000	0.785
NdCl ₃	2.65	820	0.914
	9.06	865	0.884
	17.05	930	0.822
	21.32	960	0.811
	65.81	1005	0.783
SmCl ₂	5.62	710	1.018
	13.05	825	0.912
	25.61	915	0.842
	12.58	760	0.967
	69.60	980	0.796
EuCl ₃	6.92	680	1.050
	54.49	780	0.948
	73.50	830	0.905
	85.50	915	0.842
GdCl ₃	0.72	685	1.043
	4.89	775	0.955
	37.21	910	0.845
	363.50	1015	0.777
TbCl ₃	5.41	825	0.912
	17.00	860	0.882
	27.52	950	0.817
	142.50	1040	0.761
DyCl ₃	5.43	750	0.976
	45.80	850	0.889
	15.03	805	0.931
	253.20	950	0.817
HoCl ₃	2.73	770	0.958
	25.32	870	0.874
	107.90	925	0.834
	209.00	950	0.817
ErCl ₃	6.48	770	0.958
	11.16	830	0.906
	62.80	975	0.802
	120.50	1010	0.778
TmCl ₃	7.48	800	0.932
	55.40	900	0.852
	532.00	955	0.816
	28.50	830	0.906
YbCl ₃	13.17	875	0.873
	33.21	920	0.838
	41.60	945	0.822
	231.90	1050	0.756
LuCl ₃	52.61	895	0.857
	89.42	915	0.842
	134.30	955	0.815

Cursory visual examination of the crucible was made; discoloration of the interior was evident, but no obvious marks of wall erosion were noticed. The cell body, crucible, and condensing sleeve were lightly sandblasted and rinsed in toluene before re-assembly and testing of each new chloride salt.

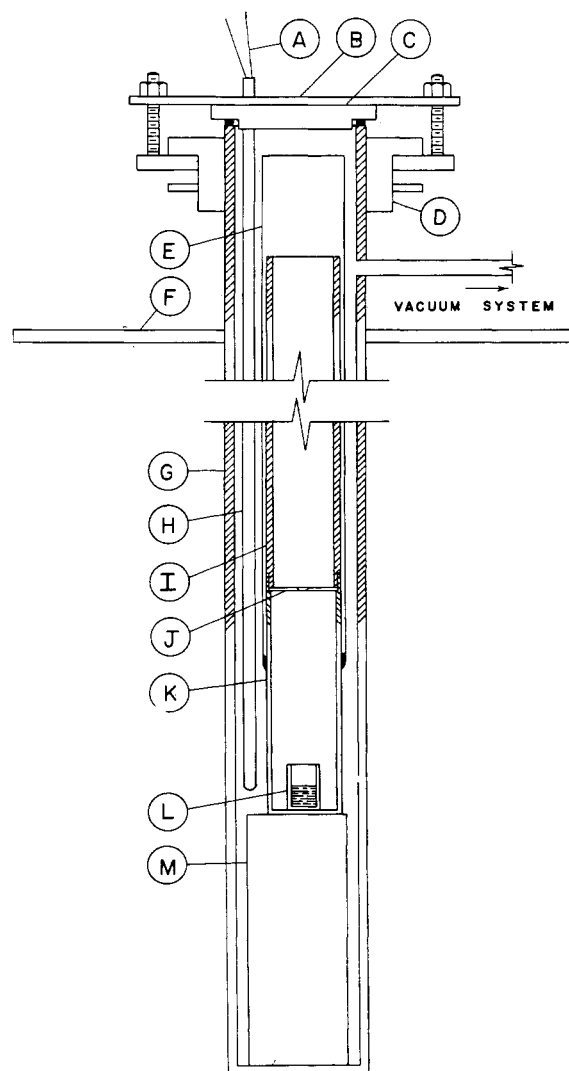


Figure 1. Effusion apparatus

- A. Chromel-Alumel thermocouple leads
- B. Pressure plate
- C. Bomb cover plate
- D. Cooling water chamber
- E. Wire handle
- F. Bomb support disk
- G. 310 S.S. bomb
- H. Thermocouple well
- I. Condensing sleeve
- J. 310 S.S. orifice plate
- K. Effusion cell
- L. 316 S.S. crucible (1½ x 1 inch i.d.)
- M. Support pedestal

RESULTS AND DISCUSSION

A plot of $\log_{10} P$ vs. $1/T$ was made from calculated pressures at a series of temperatures for each salt. More than half the salts (YCl₃, NdCl₃, SmCl₂, EuCl₃, TbCl₃, DyCl₃, TmCl₃, YbCl₃) were run in duplicate experiments using freshly prepared chlorides, with measurements made at several temperatures during each experiment. Linear graphs were made by drawing the best-fitting line through the data. The number of data points varied from three to seven depending on the number of experiments per salt. The vapor pressure empirical data are shown in Table I.

Vapor pressures, heats of vaporization, and some physical constants are shown in Table II. In some cases, the temper-

Table II. Vapor Pressures, Heats of Vaporization and some Physical Constants of Rare Earth Chlorides

Compound	Appearance	Crystal Structure (3, 7)	M.P., °C. (5)	B.P., °C. (1)	Temperature (°C.) for Vapor Pressure (mm. of Hg)					Est. ΔHv^d , Kcal./mole (1)
					4 mm.	2 mm.	1 mm.	0.1 mm.	2 mm.	
YCl ₃	white	...	709	1510	1050	975	909	735	950	30.9
LaCl ₃	white	hex. ^a	862	1750	1027	997	969	886	1100	78.9
CeCl ₃	white	hex.	817	1730	1195	1125	1065	888	1090	40.8
	blue									
PrCl ₃	green	hex. ^a	786	1710	1144	1085	1031	878	1080	44.8
	rose									
NdCl ₃	violet	hex. ^a	758	1690	1166	1106	1048	892	1060	44.4
	red									
SmCl ₂	brown	...	562	2030	1400	1229	1087	764	1310	19.9
EuCl ₃	yellow	hex.	623 ^c	decomp.	998	930	869	703	940	30.9
GdCl ₃	white	hex. ^a	602	1580	1048	995	947	808	980	44.0
TbCl ₃	white	...	582	1550	1121	1068	1010	854	960	42.0
	yellow									
DyCl ₃	green	...	647	1530	979	939	899	779	950	48.2
	rose		720							
HoCl ₃	brown	...	705 ± 5 ^c	1510	986	953	919	827	950	62.7
			776							
ErCl ₃	pink	...	760 ± 5 ^c	1500	1155	1076	1000	809	950	32.9
	light		824							
TmCl ₃	green	...	830 ± 5 ^c	1490	951	925	899	824	940	77.5
			865							
YbCl ₃	white	...	860 ± 5 ^c	decomp.	1091	1039	994	(856) ^b	940	47.7
LuCl ₃	white	...	925	1480	998	959	926	(819) ^b	950	57.2

^a Examined with X-ray diffraction powder techniques. ^b Extrapolated value below M.P.

^c Determined in this study. ^d Calculated from log P vs. $1/T$ plots.

^e Handbook of Chemistry & Physics.

ature tabulated for the 4 mm. of Hg and 2 mm. of Hg pressures represent values obtained by a linear extrapolation based on lower temperature data. Using the Clausius-Clapeyron relationship, the heats of vaporization were calculated from the slope of the curve for each salt. Comparison of the estimated 2-mm. vapor pressure temperatures (1) with the corresponding experimentally determined temperatures shows reasonable agreement in most cases. Considering the relatively small number of pressure determinations and the experimental method employed, the values presented in Table II cannot be taken as absolute. However, the vapor pressures determined during this study have been successfully used by the author to establish conditions for industrial production. Therefore, in view of the lack of published experimental information on the vapor pressures of the rare earth chlorides, it is thought that the results reported should be of practical importance in applied chemistry.

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