The phase separation temperature of an equimolar mixture fell by 2° C over a period of several weeks. However, since the measurements recorded here were taken within a few hours of preparation of each mixture, the effect of this on the results is probably negligible.

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Vapor Pressure of Cesium Metaborate

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Transpiration vapor pressure measurement over stoichiometric $CsBO_2$ (I) has been reported for the temperature range 1038–1361° K. The ΔH_v°, calculated from the slope of log P vs. $1/T$ plot was 41.3 ± 4 kcal/mol and the entropy of evaporation 23.5 cal/mol/° K.

This work was undertaken as a preliminary to the study of the effect of B_2O_3 on volatilization of cesium from cesium borosilicate melts. Among the alkali metaborates, lithium (*2, 6*), sodium (*2, 4*), and rubidium (*1*) metaborates have been studied by other authors. The only vapor species in equilibrium with cesium metaborate melt is known to be the monomeric $CsBO_2$ (*3*). This paper reports the transpiration vapor pressure measurement in the temperature range 1038–1360°K.

EXPERIMENTAL

All the precautions needed to get dependable results by the transpiration method, as discussed by Merten (*8*), were considered in designing the setup. It consisted of a sintered impervious alumina tube closed at one end with a 0.1-mm thick platinum foil bound tightly around a circular grooved cut near one extremity of the tube. A fine hole (0.5-mm diameter) was made at the center of the foil. The alumina tube was lined inside with platinum. Used were Kanthal A_1-wound tube furnace and a stepless temperature controller capable of controlling furnace temperature to within ±1° C. Temperature was measured with a platinum-platinum 13% rhodium thermocouple calibrated at the diopside point (1393° C). Temperature measurement was done with a null point potentiometer, and the cold junction of the thermocouple was maintained at 0° C with melting ice.

Dry pure nitrogen, with a maximum water and oxygen content of 0.6 and 10 ppm in volume, was used as carrier gas.

MATERIALS

An analytical reagent cesium carbonate solution was labeled with ^{134}Cs radiotracer. The solution was standardized after cesium estimation by the perchlorate method (*5*). Specific activity was calculated after gamma counting.

The B_2O_3 was prepared by fusing boric acid and maintaining it at 1000° C for 1 hr to remove traces of water. It was stored over P_2O_5.

Cesium metaborate samples were prepared by fusing together appropriate amounts of Cs_2CO_3 and B_2O_3 in a platinum boat until the evolution of gas ceased. On cooling, a needle-shaped brown crystalline (*7*) mass was obtained. When the composition accidentally became slightly rich in B_2O_3, a glassy product was produced.

Evaporation runs were made in small platinum boats. The amount of material carried away by the carrier gas was determined by gamma counting of the sample before and after the run using a NaI (Tl) scintillator under integral counting conditions. Both the γ-peaks of ^{134}Cs (0.60 and 0.80 Mev) were included in counting with a suitable discriminator setting. Statistical error due to counting was within 2% standard deviation. Background count was taken for a sufficiently long period so that error due to background was small.

The gas flow rate was determined by the pressure drop across a capillary. Gas flow rate was periodically checked during the experiment by collection of N_2 over water. Error due to water vapor in the collected gas was small. Ten measurements for a mean flow rate of 80 cc/min gave a standard deviation of ±0.8 cc.

For vapor pressure measurement at each temperature, experiments were done at different flow rates of the carrier gas. Those determinations which yielded a straight-line pass through the origin in the flow rate vs. activity-lost plot were considered for calculation of the vapor pressure (*8*) (Figure 1).

RESULTS AND DISCUSSION

Results are shown in Table I. Vapor pressure at a given temperature was calculated:

$$P_v \text{ (atm)} = \frac{m_v}{MV} RT \qquad (1)$$

where

P_v = vapor pressure in atmosphere
m_v = mass of vapor carried away by the carrier gas
M = molecular wt of the vapor ($CsBO_2$)
V = volume of carrier gas at temperature T
RT = gas constant and experimental temperature in ° K

Measurements were made above the melting point of cesium metaborate (732° C) (*7*). A least-squares fit line

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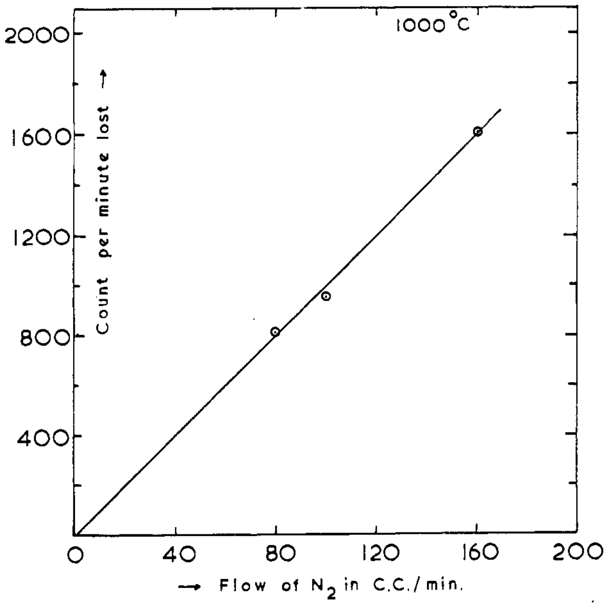

Figure 1. Plot of activity lost vs. flow of N_2

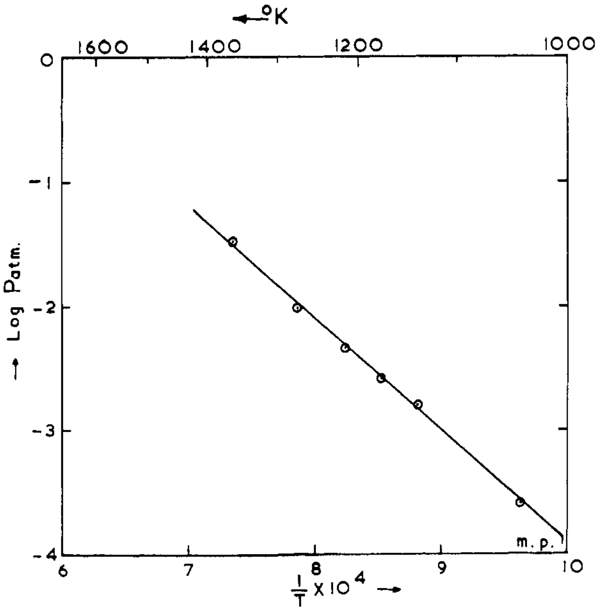

Figure 2. Plot of log *P* atm vs. 1/*T*

obtained in log *P* (atm) vs. 1/*T* plot is shown in Figure 2. The slope of the curve, according to the integrated form of the Clapeyron-Clausius equation is equal to $\Delta H°/2.303\ R$ from which the heat of evaporation can be calculated. For the reaction

$$CsBO_2\ (l) \rightleftarrows CsBO_2\ (v) \qquad (2)$$

ΔH_v° was 41.35 ± 4 kcal/mol.

The vapor pressure equation can be written as

$$\log P\ (\mathrm{atm}) = 5.129 - 9038/T\ (1038) < T < 1361) \qquad (3)$$

Table I shows the second law of heat of evaporation calculated by using the integrated Clapeyron-Clausius equation between two temperatures and two pressures. The error indicated for the enthalpy value is equal to twice the variance of the mean.

Table I. Vapor Pressure over Stoichiometric $CsBO_2$ (l)

Temp, °K	Vapor pressure, atm	$\Delta H_v^\circ\ (t_1t_2)$, kcal/mol	Mean ΔH_v°, kcal/mol
1038	$(2.54 \pm 0.07) \times 10^{-4}$		
1133	$(1.56 \pm 0.1) \times 10^{-3}$	44.75	
1173	$(2.74 \pm 0.09) \times 10^{-3}$	37.28	40.75 ± 4.3
1213	$(4.53 \pm 0.1) \times 10^{-3}$	35.55	
1273	$(9.77 \pm 0.4) \times 10^{-3}$	39.25	
1361	$(3.24 \pm 0.1) \times 10^{-2}$	46.90	

Entropy of evaporation from extrapolated boiling point works out to 23.5 cal/mol/°K.

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