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THERMODYNAMIC PROPERTIES OF SOLID BISMUTH CHLORIDES

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THERMODYNAMIC PROPERTIES OF SOLID BISMUTH CHLORIDES

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ABSTRACT

The thermodynamic stability of solid BiCl with respect to its disproportionation products, Bi(s) and $BiCl_3$ (g), has been determined from 127° to 242°C. This was accomplished by measuring the pressure of $BiCl_3$ gas over the solid subhalide and over pure $BiCl_3$ by the Knudsen technique. The pressures of $BiCl_3$ from the sublimation and disproportionation reactions are respectively:

$$\log P^{\circ}_{BiCl_3} = -\frac{6200 \pm 30}{T} + 9.95 \pm 0.07$$

and

$$\log P_{BiCl_3} = -\frac{6360 \pm 60}{T} + 9.29 \pm 0.14.$$

These results show that the subchloride is barely stable with respect to its solid disproportionation products. At 298°K the ΔH°, ΔF°, and ΔS° of formation of BiCl(s) are respectively -30.4 kcal/mole, -24.0 kcal/mole, and -18.0 e.u. New values for ΔF°_{form}, ΔS°_{form}, and S° of $BiCl_3$(s) were calculated and are respectively: -73.6 kcal/mole, -57.1 e.u., and 36.4 e.u.

I. INTRODUCTION

The bismuth chlorides consist of bismuth trichloride, $BiCl_3$, and the subhalide, BiCl. (Solid bismuth subchloride is referred to in this report as BiCl although it is possible that, like Hg_2Cl_2, the cations of this subhalide are dimerized, or form higher polymers.) The dichloride, $BiCl_2$,[1] appears to be unstable, by disproportionation,[2] while the existence of the tetrachloride[3] has not been confirmed.

Bismuth trichloride is a colorless salt, melting at 232°C and boiling at 447°C. Bismuth subchloride is not as well known. It was first isolated by Eggink[3] who determined the compound to have a chlorine to bismuth ratio of unity. At 320°C, the solid subchloride disproportionates to form two immiscible solutions, a black salt-rich phase with an overall composition of 47 mole % bismuth and 53 mole % $BiCl_3$, and a metal-rich phase consisting of 99 mole % bismuth and 1 mole % $BiCl_3$.[4] Some of the physical and chemical properties of BiCl have been described by Corbett.[5]

Recently there has been some question concerning the stability of BiCl. Brewer[2] suggested that if BiCl exists in the solid form, it is just barely stable toward disproportionation and, therefore, has about the same free energy of formation per equivalent as the trichloride. However, Sokolova,[6] who studied BiCl by X-ray techniques at room temperature concluded that it was unstable. This was based on the fact that predominant lines, which were attributed to BiCl, became quite weak 20 minutes after the compound was formed. Corbett[5] determined that BiCl was inert in dry air, and attributed Sokolova's results to excessive impurities. Therefore, it was of interest to determine the thermodynamic stability of BiCl with respect to its solid disproportionation products, Bi and $BiCl_3$.

An earlier experiment in this laboratory showed that the gas phase over solid BiCl was essentially $BiCl_3$ gas. Thus, by studying the sublimation pressure of $BiCl_3$ and the pressure of $BiCl_3$ over solid BiCl, the stability of BiCl with respect to its solid disproportionation products could be determined. Therefore, a series of vaporization experiments was carried out to determine the thermodynamic stability of BiCl. In addition to the stability of BiCl, the heat and entropy of sublimation of $BiCl_3$ and the heat of fusion of $BiCl_3$ were obtained.

The absolute entropy, the entropy and free energy of formation of solid $BiCl_3$[7] are based, in part, on the entropy of fusion[8] of $BiCl_3$. Since, as will be shown later, this value may be in error, new values for S°, ΔS°_{form}, and ΔF°_{form} of $BiCl_3$ were calculated using the sublimation data.

II. EXPERIMENTAL

A. MATERIALS

Reagent grade bismuth was melted under an inert atmosphere and filtered through Pyrex glass wool to remove bismuth oxide. Reagent grade bismuth trichloride was dried under a current of HCl gas, and distilled under HCl then under argon. The first and last eighths of the distillate were discarded. The salt had a melting point of 232.2°C. A bismuth and chlorine analysis of the salt showed a 66.2 ± 0.1 weight percent bismuth as compared to 66.27% theoretical.

Bismuth subchloride, free of $BiCl_3$, could not be synthesized simply by direct combination of $BiCl_3$ with excess bismuth, which was also noted by Corbett.[5] Therefore, the excess $BiCl_3$ was removed by sublimation. The BiCl used in this investigation was prepared from a mixture originally consisting of 80 mole % bismuth and 20 mole % $BiCl_3$, heated in a sealed Pyrex tube and continuously mixed for two days at 305°C. This process converted approximately 85% of the $BiCl_3$ into BiCl. Most of the unreacted bismuth "lumps" were mechanically removed. Since one of the products of the reaction studied was solid bismuth, it was not necessary to completely remove the unreacted bismuth.

B. PRESSURE MEASUREMENTS

The vapor pressure of solid $BiCl_3$ at the temperatures of interest is in the range where the effusion technique is applicable. The experimental apparatus was similar to that used by Farber and Darnell,[9] in their study of the lower halides of titanium. In that and in this work, a small portable dry box was attached to the vacuum manifold. Thus, the material studied was never exposed to the atmosphere. The effusion cells in this study were made of Pyrex glass 1.5 cm in diameter by 4.5 cm in length. The lids were also of Pyrex except in the case where a very small orifice was desired, in which case a platinum lid, sealed to the cell with AgCl, was used. Orifice areas were measured with a microscope and were also calibrated by vaporization of mercury. Temperatures were measured with a chromel-alumel thermocouple inserted in a thermocouple well in the cell. The quantity of effused material was determined from the weight loss of the cell contents during each run.

Pressures of $BiCl_3$ were calculated by the Knudsen equation[10] which included a Clausing[11] factor to correct for the nonideality of the orifice. Since $BiCl_3$ gas is known to be essentially monomeric,[12] 315 was used as the molecular weight.

Initially, due to the presence of excess $BiCl_3$, the vapor pressure of the mixture was equal to that obtained for pure $BiCl_3$. When about 15% of the material in the cell had effused, the pressure became constant at a value approximately one tenth that of pure $BiCl_3$. X-ray diffraction patterns of the material remaining in the Knudsen cell showed a new set of lines which agreed with the pattern of BiCl obtained by Corbett[5] but disagreed with the pattern reported by Sokolova[6] et al. The assumption that $BiCl_3$ was the predominant gaseous species was verified by determining a Cl/Bi ratio of the effusate and by comparing weight of the effusate with the weight loss of the sample. The results indicated that the gas consisted of more than 99% $BiCl_3$.

Within the experimental error, the pressures obtained for the disproportionation process were independent of orifice area, thus indicating that equilibrium pressures were attained in the cell.

III. RESULTS

The results for the pressures of $BiCl_3$ for the sublimation and disproportionation processes are shown in Tables I and II and in Figure 1.

TABLE I

SUBLIMATION PRESSURE OF $BiCl_3$

$BiCl_3(s) \longrightarrow BiCl_3(g)$, orifice area = 0.0152 cm^2, and Clausing factor = 0.51.

Temperature (°K)	Time Interval (sec)	Weight Loss (gm)	Pressure (atm)
371	4.10×10^5	0.0247	1.90×10^{-7}
394	5.76×10^4	0.0280	1.58×10^{-6}
395	1.56×10^5	0.0776	1.62×10^{-6}
415	7.25×10^4	0.2172	9.98×10^{-6}
416	4.72×10^4	0.1548	1.09×10^{-5}
416	7.50×10^4	0.2333	1.04×10^{-5}
435	4.14×10^3	0.0589	4.85×10^{-5}
435	3.90×10^3	0.0572	5.00×10^{-5}
456	4.68×10^3	0.3110	2.32×10^{-4}
457	4.08×10^3	0.2717	2.33×10^{-4}
468	4.38×10^3	0.6446	5.21×10^{-4}

A least squares analysis of the sublimation pressure $(P^\circ_{BiCl_3})$ data and of the disproportionation pressure (P_{BiCl_3}) data yielded respectively:

$$\log P^\circ_{BiCl_3} = -\frac{6200 \pm 30}{T} + 9.95 \pm 0.07 \qquad (371 \text{ to } 468°K) \qquad \ldots(1)$$

and

$$\log P_{BiCl_3} = -\frac{6360 \pm 60}{T} + 9.29 \pm 0.14 \qquad (400 \text{ to } 515°K) \qquad \ldots(2)$$

TABLE II

PRESSURES OF $BiCl_3$ FROM DISPROPORTIONATION OF BiCl(s)

$3BiCl(s) \longrightarrow 2Bi(s) + BiCl_3(g)$,

a. orifice area = 0.0152 cm^2 and Clausing factor 0.513

b. orifice area = 0.0227 cm^2 and Clausing factor 0.700

c. orifice area = 0.00208 cm^2 and Clausing factor 0.952

Temperature (°K)	Time Interval (sec)	Weight Loss (gm)	Orifice	Pressure (atm)
400	2.36×10^5	0.0178	a	2.47×10^{-7}
412	4.54×10^4	0.0136	a	9.93×10^{-7}
419	8.46×10^4	0.0359	a	1.42×10^{-6}
419	8.01×10^4	0.0310	a	1.30×10^{-6}
427	5.90×10^4	0.0775	b	2.16×10^{-6}
429	5.58×10^4	0.0464	a	2.82×10^{-6}
431	7.45×10^4	0.1299	b	2.89×10^{-6}
437	6.11×10^4	0.2117	b	5.78×10^{-6}
437	6.00×10^4	0.0919	a	5.24×10^{-6}
446	4.82×10^4	0.1543	a	1.11×10^{-5}
446	1.08×10^4	0.0299	a	9.56×10^{-6}
449	5.40×10^4	0.0700	c	1.76×10^{-5}
457	5.28×10^4	0.3968	a	2.62×10^{-5}
458	4.56×10^3	0.0358	a	2.75×10^{-5}
459	4.80×10^3	0.0366	a	2.67×10^{-5}
461	8.70×10^3	0.0756	a	3.05×10^{-5}
473	6.06×10^3	0.1218	a	7.15×10^{-5}
474	2.40×10^3	0.0453	a	6.72×10^{-5}
493	1.06×10^4	0.1933	c	2.59×10^{-4}
515	3.54×10^3	0.2347	c	9.64×10^{-4}

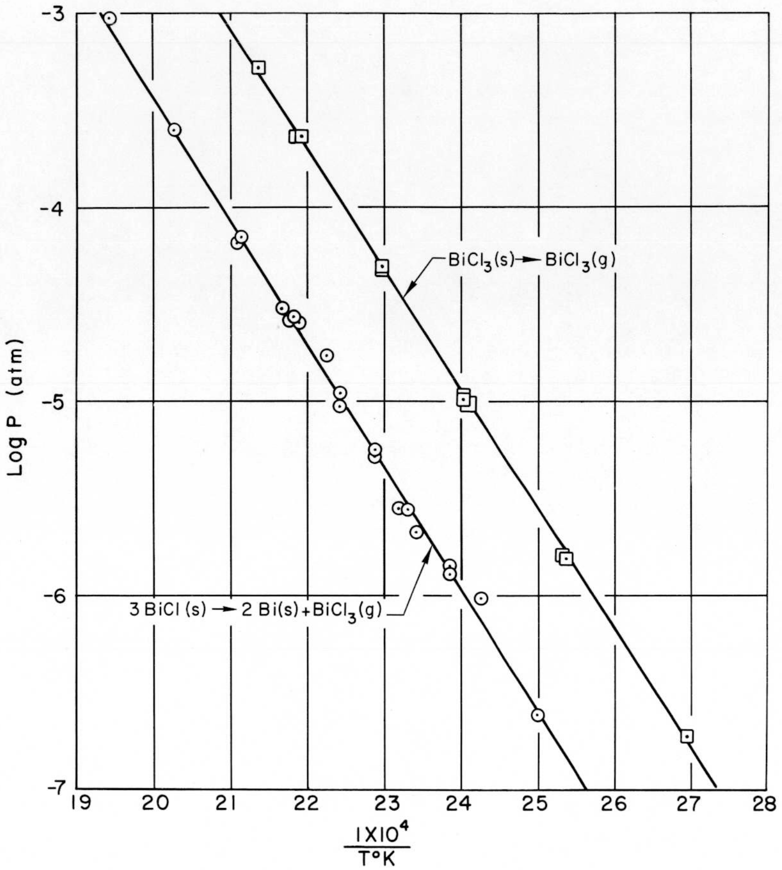

Figure 1. Pressure of BiCl$_3$ From the Sublimation of BiCl$_3$ and the Disproportionation of BiCl

The heat and entropy of sublimation for solid BiCl$_3$ was calculated from equation (1) to be 28.4 ± 0.1 kcal/mole and 45.2 ± 0.3 e.u. respectively.

In order to obtain the heat of fusion of BiCl$_3$, the heats of sublimation and vaporization were calculated at the melting point. Applying a ΔC_p estimate[13] of -10.4 to the heat of sublimation obtained in this work (28.4 kcal at the mid-temperature, 420°K) yielded a value of 27.3 kcal at the melting point. Applying a ΔC_p of -12.8[13] to the heat of vaporization (20.4 kcal[12] at 533°K) resulted in a value of 20.8 kcal. Thus, the resulting heat of fusion of BiCl$_3$ is 6.5 kcal/mole.

The absolute entropy of solid BiCl$_3$ at 298°K was calculated from the absolute entropy of the gas ($S° = 85.5$[14] e.u.) and the entropy of sublimation of BiCl$_3$ at 298°K ($\Delta S_{subl} = 49.1$). The latter was obtained by applying a ΔC_p

correction of -10.4 to the entropy obtained from equation (1). Combining the value of the absolute entropy of solid BiCl$_3$ $(S^\circ_{BiCl_3} = 36.4\ e.u.)$ with the absolute entropy of solid bismuth and chlorine gas[15] yields an entropy of formation of BiCl$_3$ of -57.1 e.u. The free energy of formation of solid BiCl$_3$ was calculated from Thomsen's[16] value for the heat of formation of solid BiCl$_3$ $(\Delta H^\circ_{form} = 90.6\ kcal)$ to be -73.6 kcal/mole.

Assuming no solid solution between Bi and BiCl, the stability of BiCl(s) with respect to Bi(s) and BiCl$_3$(s) can be determined from the following considerations:

$$BiCl_3(s) \rightleftharpoons BiCl_3(g), \qquad \Delta F^\circ_{subl} = -RT\ ln\ P^\circ_{BiCl_3}\ ; \qquad ...(3)$$

and

$$3BiCl(s) \rightleftharpoons 2Bi(s) + BiCl_3(g), \qquad \Delta F^\circ_{reac} = -RT\ ln\ P_{BiCl_3}\ . \qquad ...(4)$$

By subtracting (3) from (4) we obtain

$$3BiCl(s) \longrightarrow 2Bi(s) + BiCl_3(s), \qquad \Delta F^\circ_{disprop} = RT\ ln \frac{P^\circ_{BiCl_3}}{P_{BiCl_3}}\ . \qquad ...(5)$$

Therefore, the standard free energy change per chlorine for (5), i.e., the standard free energy of disproportionation $(\Delta F^\circ_{disprop})$ of BiCl(s) to 2/3Bi(s) and 1/3BiCl$_3$(s), is:

$$\Delta F^\circ_{disprop} = 1/3\Delta F^\circ_{form\ BiCl_3(s)} - \Delta F^\circ_{form\ BiCl(s)} = 1.53T\ log \frac{P^\circ_{BiCl_3}}{P_{BiCl_3}}\ . \qquad ...(6)$$

Substituting (1) and (2) in (6),

$$\Delta F^\circ_{disprop} = (0.245 \pm 0.102) + (0.00101 \pm 0.00024)T\ kcal/BiCl. \qquad ...(7)$$

The enthalpy of the reaction of 1 mole of solid BiCl to yield solid Bi and solid $BiCl_3$ is obtained by the usual $(\partial \Delta F/T)/(\partial 1/T)$ and is 0.245 ± 0.102 kcal while the entropy of the above reaction is obtained from the equation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = -1.01 \pm 0.24 \ e.u. \qquad \ldots(8)$$

The thermodynamic values for the disproportionation reaction at the mid-temperature, ~450°K are:

$$\Delta F^\circ_{450^\bullet K} = 0.700 \pm 0.144 \ kcal/BiCl, \qquad \ldots(9)$$

$$\Delta H^\circ_{450^\bullet K} = 0.245 \pm 0.102 \ kcal/BiCl, \qquad \ldots(10)$$

and

$$\Delta S^\circ_{450^\bullet K} = -1.01 \pm 0.24 \ e.u./BiCl. \qquad \ldots(11)$$

If the small heat capacity correction ($\Delta Cp \sim 0.1 \ cal/mole/deg$) is neglected, the value at 298°K obtained becomes

$$\Delta F^\circ_{298} = 0.546 \pm 0.125 \ kcal/BiCl, \qquad \ldots(12)$$

the other values being unchanged.

Using the above data for the formation of $BiCl_3$, the formation of 1 mole BiCl from the elements at 298°K, was calculated, and the results are compared with those of $BiCl_3$ in Table III.

TABLE III

THE FORMATION OF SOLID BISMUTH HALIDES

	$\Delta F^\circ_{form\text{-}kcal}$	$\Delta H^\circ_{form\text{-}kcal}$	$\Delta S^\circ_{form\text{-}e.u.}$
1/3 $BiCl_3$	-24.5	-30.2	-19.0
BiCl	-25.0	-30.4	-18.0

IV. DISCUSSION OF RESULTS

The $BiCl_3$ sublimation pressure reported in this work is considerably lower than that of Maier,[17] who measured the pressure of both liquid and solid $BiCl_3$ by a static method. However, his values for the vapor pressure of liquid $BiCl_3$ in the lower temperature region (below 340 °C) are considerably higher than those of other workers,[12, 18] and thus, it is reasonable to suspect that his sublimation pressures are too high. The vapor pressure obtained by extrapolation of equation (1) to the melting point (4.68×10^{-3} atm at 232 °C) is in good agreement with the pressure obtained from the extrapolation of the data of Cubicciotti[12] et al., for the liquid (4.80×10^{-3} atm at 232 °C). The equation of Kelley[19] gives 3.93×10^{-3} atm. at this temperature.

Since the heat of fusion of $BiCl_3$ was the difference of two large numbers, this value is admittedly inexact. Nevertheless, this number is considerably greater than the value of 2.6 kcal/mole accepted in the literature.[2,8] However, the latter value was selected[8] on the basis of phase diagrams of systems consisting of $BiCl_3$ and solutes, such as bismuth, ferric chloride, and cuprous chloride. The heat of fusion of $BiCl_3$ was calculated with certain assumptions as to the identity of these species. Preliminary cryoscopic experiments with different solutes, carried out in this laboratory, indicate that the heat of fusion of $BiCl_3$ lies between these extreme values.[20]

It appears that BiCl, as Brewer[2] suggested, is just barely stable toward disproportionation and has indeed about the same free energy of formation per chlorine as solid $BiCl_3$. While the thermodynamic values for the disproportionation of BiCl have large uncertainties relative to the small values, these uncertainties are quite small relative to the values for the formation of the subhalide from the elements. Thus, the accuracy for the formation values for BiCl is limited to the accuracy of the formation values of $BiCl_3$. A repeat of Thomsen's calorimetric determination or a determination of the ΔF°_{form} of $BiCl_3$ by an independent method would be desirable.

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