Heat of Formation of Beryllium Chloride

C. J. THOMPSON, G. C. SINKE, and D. R. STULL
Thermal Laboratory, The Dow Chemical Co., Midland, Mich.

BERYLLIUM and its compounds are of increasing interest in such fields as rocket propellants and nuclear reactors. Thermodynamic information on beryllium compounds is essential for these applications, but existing data are few and often of uncertain accuracy. Johnson and Gilliland (*2*) have recently measured the heat of formation of beryllium chloride by direct reaction of beryllium and chlorine. We have determined the heats of solution of beryllium metal and beryllium chloride in hydrochloric acid and agree with the result of Johnson and Gilliland within the limits of experimental error.

EXPERIMENTAL

Beryllium metal was obtained from Amend Drug and Chemical Co. in the form of small pellets. Spectroscopic examination indicated 0.1% iron, 0.15% magnesium, 0.15% silicon, and negligible amounts of other metals. Beryllium chloride was furnished by the Dow Beryllium Laboratory. It had been purified by sublimation and analyzed as 11.2% Be and 88.5% Cl (theory 11.28% Be and 88.72% Cl).

The heats of solution in hydrochloric acid were measured in a rotating bomb calorimeter. A platinum-lined combustion bomb of 345 ml. volume was used. The calorimetric system was calibrated with National Bureau of Standards benzoic acid 39h. The heat of combustion of the acid with all products and reactants in their standard states was taken as 6313.0 cal. gram^{-1} and corrections to actual bomb conditions were made using the outline of Prosen (*3*). The bomb was charged with 30 atm. of oxygen and 20 ml. of water and the initial temperature was 23° C. The cotton thread fuse had the composition $C_6H_{10}O_5$ and a heat of combustion of 3800 cal. gram^{-1}. Between the metal and the chloride experiments, some changes were made in the system, necessitating recalibration. For each calibration, the average values of q(BzOH), the heat due to benzoic acid; q(fuse), heat due to the fuse; $q(HNO_3)$, the heat due to the formation of nitric acid; q(Washburn), the correction to actual bomb conditions; Δt, the corrected temperature rise in ° C. and C, the energy equivalent in calories per degree are given in Table I. The standard deviation for each calibration is also given.

Temperatures were measured with a Western Electric Type 14B thermistor which was calibrated by comparison with a mercury thermometer which had been calibrated at the National Bureau of Standards. The variation of resistance with temperature over the range 22° to 26° was fit by a quadratic equation which was used to convert the resistance measurements to temperatures. This was necessary because the heat of solution experiments covered smaller temperature ranges than the calibration runs, and the thermistor resistance is not linear with temperature.

The metal solution experiments were run by adding 30 ml. of 6.0NHCl instead of 20 ml. of water to the bomb and placing the beryllium pellets in a platinum crucible suspended from the bomb lid. The bomb was closed and thoroughly flushed with nitrogen. The bomb was then placed in the calorimeter and reaction began when rotation was started, dumping the metal into the acid. The calorimeter equivalent was corrected for the removal of the 20 ml. of water, 30 atm. of oxygen, and 20 grams of platinum parts not used in the solution experiments and the addition of the 30 ml. of 6.0NHCl and the beryllium. The heat capacity of 6.0NHCl was measured as 0.715 cal. gram^{-1} ° C.$^{-1}$ for this calculation. Results were corrected for impurities using data from Rossini, Wagman, Evans, Levine, and Jaffe (*4*) and are given in Table II.

The beryllium chloride was handled only in a dry box because of its hygroscopic nature. A sealed-off, thin-walled glass ampoule of approximately 30 ml. volume and filled with 4.7NHCl was placed in the bomb along with a weighed sample of the chloride and the bomb closed while still in the dry box. The bomb was transferred to the calorimeter and reaction was initiated when rotation started, breaking the ampoule. The concentration of HCl and the size of the $BeCl_2$ samples were such that the final solution was identical to that of the Be metal experiments. The calorimeter equivalent was calculated for each experiment, using heat capacities of 0.776 cal. gram^{-1} ° C.$^{-1}$ for 4.7NHCl, 0.15 cal. gram^{-1} ° C.$^{-1}$ for glass, and 0.2 cal. gram^{-1} ° C.$^{-1}$ for $BeCl_2$. The HCl heat capacity was interpolated from the Dow value for 6.0NHCl and the results of Gucker and Schminke (*1*). Results are given in Table III. The vaporization correction is due to vaporization of water into the dry atmosphere of the bomb when the ampoule is broken.

RESULTS

Atomic weights of 9.013 and 35.457 for Be and Cl, respectively, were used to calculate molar heats of reaction. The Be experiments were corrected to constant pressure by the relation $\Delta H = \Delta E + \Delta nRT$, in which Δn is the increase in moles of gas in the reaction. The heat of dilution of HCl at 25° C. was taken from Rossini, Wagman, Evans, Levine,

Table I. Benzoic Acid Calibration Experiments

q(BzOH)	q(fuse)	$q(HNO_3)$	q(Washburn)	Δt, ° C.	C, Cal. ° C.$^{-1}$
For Metal Experiments					
6901.71	9.67	2.13	15.15	2.03623	3402.68
					Std. dev. of 7 expt. = 0.82
For $BeCl_2$ Experiments					
6816.98	8.42	1.75	14.97	2.00797	3407.48
					Std. dev. of 5 expt. = 0.28

Table II. Heat of Solution of Beryllium in 6.0NHCl

Sample Mass, G.	Net Mass Be, G.	C, Cal. ° C.$^{-1}$	Δt, ° C.	Impurity Corr., Cal.	$-\Delta E/M$, Cal. G.$^{-1}$
0.19859	0.19780	3403.35	0.58222	2.19	10,007
0.19219	0.19142	3403.35	0.56334	2.19	10,004
0.19550	0.19472	3403.35	0.57339	2.19	10,011
0.19460	0.19382	3403.35	0.57096	2.19	10,014
				Av.	10,009

Table III. Heat of solution of Beryllium Chloride in 4.7NHCL

Sample Mass, G.	Wt. HCl, G.	Vaporization Corr., Cal.	C, Cal. ° C.$^{-1}$	Δt, ° C.	$-\Delta E/M$ Cal. G.$^{-1}$
1.6862	30.45	2.93	3409.72	0.28243	572.85
1.8416	33.59	2.93	3412.36	0.30905	574.24
1.8295	33.09	2.93	3411.81	0.30825	576.45
				Av.	574.51

and Jaffe (*4*). The average temperature of reaction was 24.4° C. and the heat of dilution was corrected to this temperature using the heat capacity data cited previously. The following reaction sequence could then be set up:

	ΔH, kcal.
$Be(c) + [8.381\ HCl + 67.982\ H_2O] \rightarrow BeCl_2[\text{in aq. } HCl] + H_2(g)$	−89.62
$BeCl_2[\text{in aq. } HCl] \rightarrow BeCl_2(c) + [6.381\ HCl + 67.982\ H_2O]$	+45.92
$[6.381\ HCl + 67.982\ H_2O] + 2HCl(g) \rightarrow [8.381\ HCl + 67.982\ H_2O]$	−30.43

Combining algebraically	ΔH, kcal.
$Be(c) + 2HCl(g) \rightarrow BeCl_2(c) + H_2(g)$	−74.13

A very small correction of 4 cal. $mole^{-1}$ $deg.^{-1}$ was applied to bring this result to 25° C., which was then combined with −22.063 kcal. $mole^{-1}$ for the heat of formation of HCl(g) to derive for $BeCl_2(c)$

$$\Delta H_{f\,298}(c) = -118.25 \text{ kcal. mole}^{-1}$$

The over-all uncertainty is estimated as ±0.50 kcal. $mole^{-1}$. Johnson and Gilliland found −118.03 ± 0.56 by direct reaction of beryllium and chlorine. The agreement of the two methods is very satisfactory and establishes the heat of formation of beryllium chloride within considerably narrower limits than the older literature values allowed.

LITERATURE CITED

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Heats of Reaction of Halogenated Ethanes on Graphite

RICHARD F. PORTER and DAVID H. SMITH
Department of Chemistry, Cornell University, Ithaca, N. Y.

LOW PRESSURE reactions between graphite and dichloro derivatives of ethane with chlorine atoms in the 1,2 positions have been the subject of a recent investigation (*1*). It has been proposed that the reaction involves the transfer of chlorine atoms from the gaseous reactants to the graphite,

$$CR_2Cl{-}CR_2Cl + \text{graphite} = CR_2{=}CR_2 + 2Cl\ (\text{Graphite})$$

where R can be H, Cl, or F. The main experimental features of this reaction are the first order pressure dependence of product on reactant and the appearance of HCl(g) as the only other observable product.

This article is an extension of work described previously and includes an examination of the reaction of $CF_2Br{-}CF_2Br$ on graphite. An attempt to arrive at a more quantitative interpretation of the results has also been made.

EXPERIMENTAL

The mass spectrometer and high temperature assembly for vaporization studies and recent modifications to the original apparatus have been described (*1*, *7*). A further modification of the apparatus was introduced to allow investigations of solids with low vapor pressures (C_2Cl_6) in a method similar to that previously used only in gases and volatile liquids (Figure 1). For reactions of the dichloro compounds, reaction vessels constructed from an electrolytic grade of graphite were employed. For reactions with $CF_2Br{-}CF_2Br$ an oven made of pyrolytic-grade graphite was also used. With the present apparatus it is possible to control the leak rate and reaction pressure and temperature independently. Some care had to be taken in selecting a

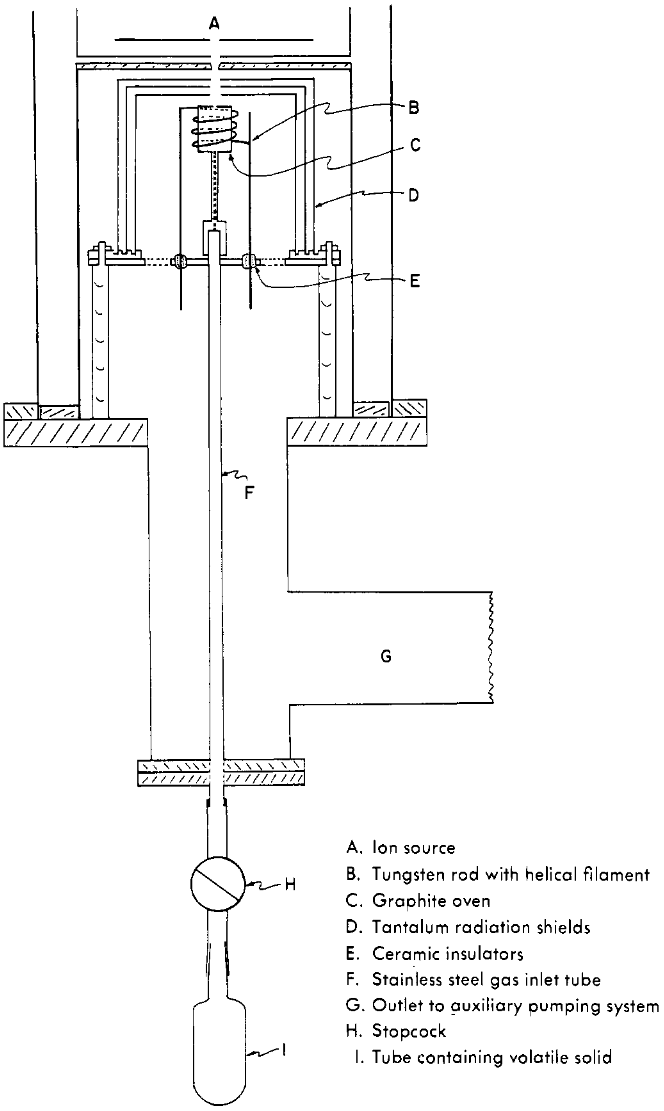

Figure 1. Mass spectrometer furance assembly and gas inlet system