amines does not mean that F-strain is absent. Indeed, the results previously reported[24] show that F-strain must be present. However, it probably increases regularly with the introduction of one, two or three methyl groups into the amine. The absolute magnitudes of the amine strengths are thus affected; their relative order, however, is not altered.

The proposed explanation leads to a number of interesting predictions; these are now being tested.

Acknowledgment.—The authors express their appreciation to Professors G. N. Lewis, R. S. Mulliken and Linus Pauling for their kindness in examining the manuscript and for their helpful suggestions.

Summary

1. The trimethylboron addition compounds with ammonia, methylamine, dimethylamine and trimethylamine have been prepared and characterized.

2. The dissociation of these compounds in the vapor phase ($R_3N:BMe_3 \rightleftarrows R_3N: + BMe_3$) has been studied; ΔH, ΔF and ΔS for the reactions have been measured.

3. The relative affinity of the methylamines for trimethylboron (measured by the dissociation constant of the complex) is identical with their affinity for the proton (measured by the dissociation constant of the base). In both instances, the base strength rises from ammonia to methylamine and to dimethylamine, but drops sharply from dimethylamine to trimethylamine.

4. To account for this observed order the strain resulting from the "steric factor" is divided into two kinds, "B-strain" and "F-strain." The anomalous behavior of the methylamines is ascribed to B-strain.

CHICAGO, ILLINOIS　　　　　　RECEIVED AUGUST 7, 1943

The Vapor Pressure of Beryllium at 1170-1340°K.

BY ROBERT SCHUMAN AND A. B. GARRETT

The vapor pressure of beryllium was determined by measuring the rate of vaporization in a vacuum. The theory and application of this method are adequately described by other investigators.[1,2,3,4] In the case of beryllium, the accommodation coefficient appears (qualitatively) to be unity within the limits of experimental error. This was true for iron,[2] copper,[2] nickel,[3] nickel oxide,[3] and for liquid and solid mercury.[5,6]

Experimental

The procedure was that of determining the loss of weight due to evaporation of a beryllium ring of known surface area; the ring was held at a constant known temperature by an induction furnace for a known length of time.

The beryllium was a very pure sample supplied by the Brush Beryllium Company with the analysis: 0.03% Fe, 0.008% Al, 0.004% Mg, 0.022% Si. The ring was made from the sample and had an effective area of evaporation of about 8.5 sq. cm.

The water-cooled cell was a modification of the one used by Marshall, Dornte and Norton,[2] but was made of Pyrex glass. The cell was constructed with two small-diameter water-cooled glass tubes sealed just inside the inner tube to prevent the formation of a continuous film of metal on the inside of the tube. The ring was supported by a tungsten tripod. The optical window at the top of the cell was protected from the metal vapors by a glass shutter.

The temperature was measured by a Leeds and Northrup No. 8622-C optical pyrometer with which the readings were easily reproducible to within 5°. The pyrometer was calibrated against the apparent black body temperature of

melting silver, the silver being melted in a groove in an iron ring into which small holes had been drilled to serve as black bodies. The pyrometer was checked three times against the melting point of silver, the apparent melting points having a variation of 3°. The temperature of the beryllium ring used for determining the rate of evaporation was taken as the apparent emission temperature, and then corrected to black body temperatures by values of beryllium emissivities determined. The beryllium emissivities were obtained by comparing the apparent temperature readings of a polished beryllium surface and those of 1-mm. diameter, 4-mm. deep holes drilled in the specimen.

A pressure below 10^{-5} mm. of mercury was maintained throughout the run to prevent oxidation. In several runs in which the vacuum was poor, surface oxidation prevented or slowed up evaporation. A period of outgassing at dull red heat was also found valuable to eliminate adsorbed gases.

The weighings were made on a balance accurate to about ±0.05 mg.

Data.—The experimental results are recorded in Table I and Fig. 1 for the rate of vaporization. The temperatures given are the average temperature during the runs, and thus take into account small fluctuations in temperature during the run. The times are the effective times at the temperature indicated. The apparent emission temperatures for $\lambda = 6500$ Å. are given in terms of the black body temperatures by the equation

$$t_e = 0.904 t_{bb} + 54.5 \quad (\pm 5° \ 800\text{-}1000°)$$

where t_e is the apparent polished surface temperature in °C. and t_{bb} is the corresponding black body temperature, °C. Runs 9 and 12 were of no value owing to surface oxidation.

Thermodynamic Considerations.—In order to check the validity of the vapor pressure results,

(1) Langmuir, *Phys. Rev.*, **2**, 329 (1913).

(2) Marshall, Dornte and Norton, THIS JOURNAL, **59**, 1161 (1937).

(3) Johnston and Marshall, *ibid.*, **62**, 1382 (1940).

(4) Marshall and Norton, *ibid.*, **55**, 431 (1933).

(5) Knudsen, *Ann. Physik*, **29**, 179 (1909).

(6) Volmer and Estermann, *Z. Physik*, **7**, 1 (1921).

Table I

Experimental Results

Run	T, °K., actual	Time, min.	Loss, g.	Rate of loss, g./sec./sq. cm.	log P
18	1174	217	0.00274	2.52×10^{-8}	-8.189
11	1187	180	.00138	1.52×10^{-8}	-8.405
19	1193	204	.00192	1.88×10^{-8}	-8.313
8	1215	180	.00241	2.63×10^{-8}	-8.162
6	1222	120	.00361	5.91×10^{-8}	-7.809
5	1227	121	.00517	8.38×10^{-8}	-7.655
17	1251	65	.00412	1.267×10^{-7}	-7.473
16	1259	63	.00783	2.48×10^{-7}	-7.179
1₁	1271	120	.0102ᵃ	1.644×10^{-7}	-7.356
7	1273	65	.00610	1.842×10^{-7}	-7.306
14	1273	50	.00582	2.315×10^{-7}	-7.206
10	1281	61	.00604	1.957×10^{-7}	-7.279
15	1293	40	.00998	4.97×10^{-7}	-6.871
3	1305	36	.0079ᵃ	4.28×10^{-7}	-6.935
2	1308	38	.0068ᵃ	3.49×10^{-7}	-7.023
20	1314	21	.00550	5.27×10^{-7}	-6.842
4	1326	28	.0102ᵃ	7.13×10^{-7}	-6.710
1₂	1330	22	.0100ᵃ	8.83×10^{-7}	-6.614
13	1336	14.5	.00665	9.10×10^{-7}	-6.601

ᵃ ±0.2 mg.

the values of ΔH_0^0 were calculated from values of log P and T read off from the graph of log P vs. $1/T$ (Fig. 1). The thermodynamic relationship for ΔH_0^0 is

$$\frac{\Delta H_0^0}{T} = -R \ln p - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{gas}} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}}$$

The free energy function of the gas is dependent both on the vapor pressure results and on the spectroscopic energy levels of beryllium. Any error in it is due solely to the vapor pressure data. The function is

$$\left(\frac{F^0 - H_0^0}{T}\right)_{\text{gas}} = -3/2 R \ln M - 5/2 R \ln T +$$
$$R \ln P - C - R \ln R - R \ln Q$$

For beryllium the ground state is $^1S_0$ and the next higher state is $^3P_0$ with a term value of 21981.4 cm.$^{-1}$. The second state contributes nothing to Q at the temperatures of the experiments, and the a priori probability of the ground state is 1, so, for this case, $Q = 1$. If P is measured in atmospheres, the value of $C + R \ln R$ is -7.267 (see ref. 7).

The free energy function of the solid is dependent only on specific heat data. The function is

$$\left(\frac{F^0 - H_0^0}{T}\right)_{\text{solid}} = \frac{1}{T} \int_0^T C_p \, dT - \int_0^T C_p \, d \ln T$$

The specific heats below 298°K. were those given by K. K. Kelley,[8] and the equation used for the higher range is[9]

$$C_p = 4.698 + 1.555 \times 10^{-3}T - 1.210 \times 10^5 T^{-2}$$
$$(1\%, 273\text{–}1173°K.)$$

(7) For a general discussion of the equation, see K. K. Kelley, Bureau of Mines Bulletin, 383, 1 (1935).

(8) K. K. Kelley, ibid., 434, 84 (1941).

(9) K. K. Kelley, ibid., 371, 12 (1934).

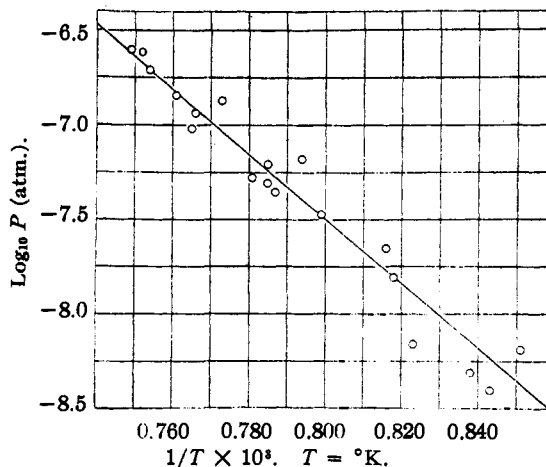In our calculations, this equation was used in a range somewhat above its upper limit of applicability.

Fig. 1.

The calculated results of ΔH_0^0 are given in Table II. The trend in the ΔH_0^0 values, a variation of 5000 cal./mole over the temperature range studied would indicate that the curve is either (a) somewhat steeper than it should be, or (b), that the trend is due to inaccuracies in C_p, since the temperature is above the range of the C_p equation. We feel, however, that the curve drawn best represents the experimental data.

Table II

Summary of Thermodynamic Calculations

T, °K.	log P (atm.)	$\frac{F^0 - H^0}{T}$ gas	$\frac{F^0 - H^0}{T}$ solid	ΔH_0^0, cal./mole
1550	-8.670	-73.966	-4.85	125,100
1200	-8.067	-71.421	-5.05	123,900
1250	-7.497	-69.016	-5.23	122,600
1300	-6.970	-66.798	-5.42	121,300
1350	-6.498	-64.826	-5.60	120,100

Other Considerations.—The log vapor pressure vs. reciprocal of temperature curve was drawn as a straight line; this plot is given in Fig. 1. The slope of the line in Fig. 1 corresponds to a heat of vaporization for beryllium of 78,800 ± 2000 cal./mole near 1250°K.

The trend in the ΔH_0^0 values might also indicate an accommodation coefficient different from unity; however, it is doubtful that it would differ enough from unity to cause as large a trend as observed. The fact that the beryllium did not deposit behind the small glass tubes in the cell would indicate a value near to unity.

The most likely sources of experimental error in this work are: first, the formation of an oxide film on the beryllium thick enough to greatly hinder the evaporation; second, inaccurately assumed temperatures due to fluctuations of temperature during the run; and also, to a lesser ex-

tent, errors in the weighings and temperature readings. Of these, the first probably caused the largest errors, since runs in which the vacuum was poor gave very erratic results (runs 9 and 12). Thinner oxide films would not stop the evaporation, but still might slow it down appreciably. However, early in the work it was recognized that this might be the main source of error; accordingly, special care was observed in all the work to reduce this error to a minimum. For results on films of nickel oxide on nickel, see the results on nickel oxide by Johnston and Marshall.[3,10] The temperature control of the furnace was not all that could be desired, and a considerable error might have been caused by temperature variations; however, this source of error was minimized by taking temperature readings at frequent intervals throughout the run. The errors by

other causes should be small in relation to these two.

Acknowledgment.—We wish to express our appreciation to the Brush Beryllium Company for the pure beryllium sample, and to Prof. H. G. Heil of the Mendenhall Laboratory of Physics, for the use of the high temperature equipment and for instructions in its use.

Summary

The vapor pressures of metallic beryllium in the range from 1170 to 1340°K. have been determined by the Langmuir method. The results are given in Table I, and a plot of log P vs, $1/T$ is given, Fig. 1. Values of ΔH_0^0 have been calculated and found to vary some with temperature, the mean value of ΔH_0^0 being (122,000 ± 2500) cal./mole. The heat of vaporization was also calculated, being 78,800 cal./mole at 1250°K. Possible sources of experimental error are considered, the slowing down of evaporation by thin oxide films probably being the most important. The accommodation coefficient appears to be unity.

Temperature Coefficients of Electrical Conductance of Solutions Containing Sodium Chloride, Potassium Chloride or Magnesium Sulfate or Mixtures Thereof

BY RAYMOND W. BREMNER

Introduction

Very little accurate information on the variation of electrical conductance with temperature is available in the literature. In this paper equations for very accurately calculating equivalent conductance as a function of centigrade temperature have been worked out. Temperature coefficients of equivalent conductance have been calculated with five-place accuracy. Temperature coefficients of specific conductance of certain standard potassium chloride solutions and of conductivity water have also been calculated. The variations of the coefficients due to temperature changes, concentration changes and mixing of electrolytes have been determined.

Calculations

Equivalent Conductance as a Function of Temperature.—Equation I was used for representing the equivalent conductances of twenty different solutions as a function of centigrade temperature.

$$\text{Eq. Cond.} = \Lambda = a + bt + ct^2 + dt^3 \qquad (I)$$

The preparation of solutions and the experimental data have been described previously.[1,2] The

(1) Raymond W. Bremner, Thomas G. Thompson and Clinton L. Utterback, THIS JOURNAL, **60**, 2616 (1938).

(2) Raymond W. Bremner, Thomas G. Thompson and C. L. Utterback, *ibid.*, **61**, 1219 (1939).

ratio of the number of millimoles of sodium chloride to the number of millimoles of magnesium sulfate in a given quantity of each of the four solutions that contain both of these salts is 16.4315. Similarly the ratio of the number of millimoles of sodium chloride to the number of millimoles of potassium chloride in a given quantity of each of the four solutions that contains both of these salts is 47.2916. The most dilute solution of each type is designated as Solution No. 1, while the most concentrated solution is designated as Solution No. 4. Solutions of intermediate concentrations are numbered 2 and 3, respectively.

The constants a, b, c and d of Equation I were evaluated from the experimental data for each solution by the method of least squares. By use of the resulting equations the equivalent conductance was calculated for each solution at 0, 5, 10, 15, 20 and 25°. The average deviation of the calculated from the experimentally determined value was only 0.006%. In no instance was the deviation greater than 0.02%, which is the approximate maximum error in the original data.

In Table I are listed the values of the constants of equation I for each solution. The constant (d), which is the coefficient of the term of highest degree, is in every instance negative. This indicates a point of inflection at a higher temperature