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Report No. BMI-1186
UC-4 Chemistry - General
(TID-4500, 13th Ed.)

Contract No. W-7405-eng-92

BMI-1186

VAPOR PRESSURE AND EQUILIBRIUM STUDIES OF THE
SODIUM FLUORIDE-BERYLLIUM FLUORIDE SYSTEM

by

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May 27, 1957

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VAPOR PRESSURES AND EQUILIBRIUM STUDIES OF THE SODIUM FLUORIDE-BERYLLIUM FLUORIDE SYSTEM

Karl A. Sense, Richard W. Stone,
and Robert B. Filbert, Jr.

A new study made on the vapor pressure of BeF_2 over the temperature interval 802 to 1025 C showed good agreement with previous data taken over the 802-968 C range. Excessive scatter of the vapor-pressure data in the lower temperature region prevented a melting-point determination of BeF_2 by the transpiration method alone. Thermal analysis showed the melting point to be about 545 C. Vapor pressures of the NaF-BeF_2 system were measured over the range 509 to 1061 C. On the basis of previously developed theory it was concluded that the complex NaBeF_3 exists in the vapor phase in addition to NaF and BeF_2 . Resolution of the vapor phase on this basis led to the disclosure that another complex must exist in the vapor phase. This additional complex was postulated as being Na_2BeF_4 . In the absence of enough equations to solve for all the unknowns, a system of partial pressures was approximated within the framework of the experimental data. This system was made self-consistent with respect to smoothed plots of the equilibrium constants as functions of temperature. A liquid-vapor phase diagram and plots showing how the total pressure varies with the composition are presented.

INTRODUCTION

This work is a continuation of the study of the physical properties of fused-salt systems which was started with the investigation of the NaF-ZrF_4 system previously reported.⁽¹⁾ In the NaF-ZrF_4 report, a theory was presented for the determination of vapor-phase molecular complexes. The report on the NaF-BeF_2 system augments the study of molecular complexes in the vapor phase.

EXPERIMENTAL PROCEDURE

Description of Method and Apparatus

The method and apparatus used have been adequately described previously.^(1,2) The only change from previous procedure consisted in improved oxygen removal from the argon which was used as a carrier gas. This was accomplished by passing the argon over heated uranium chips after most of the oxygen had been removed by heated copper turnings.

Materials

The fused salt mixtures were supplied by the Mound Laboratory at Miamisburg, Ohio, and the Oak Ridge National Laboratory at Oak Ridge, Tennessee. Table 1 is a

(1) References are listed at the end of this report.

list of mixtures used and the name of the laboratory that prepared the samples. Composition of the salt was based on numerous analyses made at Battelle.

TABLE 1. COMPOSITION OF STARTING MATERIALS

Composition		Batch (Oak Ridge Designation)	Laboratory
Mole Per Cent NaF	Mole Per Cent BeF ₂		
85.1	14.9	--	Mound
80.9	19.1	EE-741	Oak Ridge
75.6	24.4	--	Mound
68.5	31.5	EE-740	Oak Ridge
60.5	39.5	--	Mound
49.9	50.1	--	Mound
41.1	58.9	--	Mound
25.9	74.1	--	Mound

In most cases, the composition of the salt mixtures changed slightly during the runs because of the preferential vaporization of the more volatile component. Corrections were made for this effect, and the average compositions are listed on the various plots with the proper curves.

RESULTS

The Vapor Pressure of BeF₂

The vapor pressure of BeF₂ had been measured some time ago.⁽²⁾ Because the apparatus and techniques in measuring vapor pressures have been improved since publication of the original report, another set of measurements was made. The results of these measurements are treated in two parts: those obtained for temperatures greater than about 800 C and those obtained below that temperature. For temperatures greater than about 800 C, relatively little difficulty was experienced in obtaining reasonably consistent data (see Table 2). The results compare favorably with those given in the previous report.⁽²⁾ Figure 1 is a plot of the recent measurements and with the best curve* obtained, as well as the best curve obtained for the previous set of data. The new vapor-pressure curve has a somewhat flatter slope, resulting in a heat of vaporization value of

$$\Delta H_v = 50.1 \text{ kcal per g-mole} , \quad (1)$$

as compared with the old value of 50.9 kcal per g-mole. At $\frac{1}{T(K)} = 7.8 \times 10^{-4}$, the new vapor-pressure curve yields a value about 10 per cent lower than the previous one,

*In the least-square treatment, the data were weighted, since in some instances two or more analyses were made for a single run.

TABLE 2. VAPOR PRESSURES OF BeF₂

Temperature, C	Pressure, mm mercury		Deviation, per cent	Flow Rate of Carrier Gas, cm ³ per min
	Observed	Calculated		
1025	106.2a	108.6	-2.2	8.5
1010	88.9	86.3	+3.0	11.5
989.6	70.4a	63.1	+11.6	9.0
974.8	50.7b	49.8	+1.8	11.2
960.5	40.4b	39.4	+2.4	10.0
945.9	31.6a	30.9	+2.4	14.9
932.0	24.4a	24.3	+1.1	18.9
932.0	22.1b	24.3	-9.0	21.2
917.4	18.2b	18.8	-3.1	19.9
917.4	18.4a	18.8	-2.1	20.9
900.7	13.86a	13.93	-0.5	23.3
889.7	11.25a	11.37	-1.1	23.6
889.1	10.85	11.17	-2.8	23.0
877.6	8.59b	9.06	-5.2	20.2
863.0	6.94a	6.83	+1.6	20.9
850.3	5.48	5.32	+3.1	31.1
839.5	4.05a	4.28	-5.3	31.2
838.0	4.27b	4.15	+2.9	30.8
825.4	3.47	3.20	+8.5	32.4
813.9	2.70	2.51	+7.4	40.1
802.2	2.05	1.95	+5.2	41.1

Note: a = Pressure based upon average of two analyses.

b = Pressure based upon average of three analyses.

FIGURE 1. VAPOR PRESSURES OF PURE BeF_2 OVER THE RANGE 802 C TO 1025 C

Solid curve is result of weighted least-square treatment of data. Dashed curve is result of previous study.

while at $\frac{1}{T(K)} = 9.3 \times 10^{-4}$, it is only about 4 per cent lower. The revised vapor-pressure equation which holds for the temperature interval 802 to 1025 C is

$$\log p = 10.466 - \frac{10943}{T(K)}, \quad (2)$$

where p is measured in mm of mercury.

$$\text{The extrapolated boiling point} = 1170 \text{ C} . \quad (3)$$

Below about 800 C, difficulties were encountered in obtaining consistent data. In addition to the data given, 13 additional runs were made between $\frac{1}{T(K)} = 9.6 \times 10^{-4}$ (770 C) and $\frac{1}{T(K)} = 9.9 \times 10^{-4}$ (738 C). All of these runs were made with a carrier-gas flow rate of very nearly 50 cm³ per min. The oxygen was removed from the carrier gas by heated copper only. The results are given in Figure 2. No firm vapor-pressure values were obtained for these runs because analyses of the condensates showed the amount of beryllium present to be below the detection limit. The following explanation was postulated. Enough oxygen was left in the carrier gas to react with BeF₂ and form a thin film of BeO covering the BeF₂ charge. Below about 800 C, the viscosity of BeF₂ increased sufficiently that the coating of BeO remained on the surface, making it difficult for the BeF₂ molecules to vaporize. In an attempt to solve the problem, the carrier gas was passed over copper and then over heated uranium chips for further oxygen removal, and the runs were made at much lower flow rates to enhance the possibility of equilibrium conditions existing between vapor and liquid. Figure 2 shows graphically the results obtained.

Even though considerable scatter is evident for the firm data, no break in the pBeF₂ curve is evident above about 700 C. This shows the melting point of BeF₂ to be considerably lower than indicated from previous vapor-pressure work.⁽²⁾ Below about 700 C the scatter of the data permits no interpretation. It seems from these investigations that it would be difficult to obtain the melting point of BeF₂ from vapor-pressure measurements alone.

Since the scatter of the data on pure BeF₂ was excessive below about 700 C, it was considered of interest to obtain vapor-pressure data for the 26 mole per cent NaF-74 mole per cent BeF₂ composition below 700 C. It was hoped that the presence of NaF would reduce the viscosity of BeF₂ sufficiently to result in consistent vapor-pressure data. Figure 3 shows the results obtained over the 509 to 977 C range. Though the data scatter somewhat below 635 C, excessive scatter starts only below 535 C. A break in the curve is not evident above that temperature.

The Vapor Pressure of NaF

The vapor pressures of NaF have been reported previously.⁽¹⁾ Since no additional data are available, the derived P-T relations remain unchanged. From 934 to 996 C, the melting point,

$$\log p = 11.3315 - \frac{14855.7}{T(K)} . \quad (4)$$

FIGURE 2. VAPOR PRESSURES OF PURE BeF_2 OVER THE RANGE 636 C TO 814 C

Figures represent flow rates in cm^3/min of carrier gas for each run.
Curve obtained from P-T equation derived from data for 802 C to 1025 C range.

FIGURE 3. PARTIAL PRESSURES OF BeF_2 FOR 26.1 MOLE PER CENT NaF -73.9 MOLE PER CENT BeF_2 COMPOSITION OVER THE RANGE 509 C TO 977 C

From 996 to 1075 C,

$$\log p = 9.4188 - \frac{12428.3}{T(K)}, \quad (5)$$

where p is measured in mm mercury.

The Vapor Pressures of the NaF-BeF₂ System

Molecular Species in the Vapor Phase

Results of vapor-pressure runs for the NaF-BeF₂ system are given graphically in Figures 4, 5, 6, and 7 and in tabular form in Table 3. The data are presented on the basis that only NaF and BeF₂ exist in the vapor phase. The solid lines represent the best curves through these data. The dashed lines (which coincide to some extent with the solid lines) will be discussed later.

Figure 8 is a partial pressure plot of NaF and BeF₂ as a function of composition at 890 C, assuming that only NaF and BeF₂ exist in the vapor phase. Previously presented theory⁽¹⁾ based on the Duhem-Margules equation,

$$x_1 \left(\frac{\partial \ln p_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln p_2}{\partial x_2} \right)_{T,P}, \quad (6)$$

discloses that the peak of a partial-pressure curve indicates the presence of a molecular complex in the vapor phase, the composition of the complex being given by the location of the peak. In Figure 8, the peak of the p' NaF* curve is located at 50 mole per cent BeF₂. Hence, the complex is immediately determined as being NaBeF₃. In accordance with the procedure worked out previously⁽¹⁾, the partial pressures of NaF, BeF₂, and NaBeF₃ were determined for 890 C and plotted in Figure 9. From this plot the composition which melts at 890 C was determined as being 16.5 mole per cent BeF₂. This is in slight disagreement with the phase diagram by Thilo and Schröder⁽³⁾, which indicates that this is the melting point for a 15 mole per cent BeF₂ composition. Since the solid phase is NaF, p' NaF remains constant over that composition region. The dashed line above it represents the vapor pressure of the supercooled solution. However, the most interesting part of the plot is the appearance of another p' NaF peak in the NaF-NaBeF₃ system. In accordance with theory, this peak is evidence of the existence of an additional molecular complex in the vapor phase. It is clear that the peak of the p' NaF curve would have to occur between 31.5 and 50 mole per cent BeF₂. Starting with the simplest one, the complexes which could have their partial pressure peaks in that region are Na₂BeF₄, Na₃Be₂F₇, Na₄Be₃F₁₀, Since it seems unlikely that very large molecules exert an appreciable vapor pressure, the assumption is made that the complex Na₂BeF₄ exists in the vapor phase together with NaBeF₃, NaF, and BeF₂.

*To avoid confusion, partial pressures calculated on the basis that only NaF and BeF₂ exist in the vapor phase will be denoted by a double prime ("'); for a system based on the existence of NaF, BeF₂, and NaBeF₃ in the vapor phase, the partial pressures will be denoted by a single prime (''); for a vapor phase assumed to consist of NaF, BeF₂, NaBeF₃, and Na₂BeF₄, the partial pressures will be given without any primes.

FIGURE 4. PARTIAL PRESSURE OF BeF₂ ON THE BASIS THAT ONLY NaF AND BeF₂ EXIST IN VAPOR PHASE

Solid lines represent best curves through these data. Dashed lines are explained in text. Figures denote mole per cent BeF₂.

FIGURE 5. PARTIAL PRESSURES OF NaF FOR THE 24.5 TO 50.0 MOLE PER CENT BeF_2 REGION

Values based on assumption that only NaF and BeF_2 exist in vapor phase. Solid lines represent best curves through these data. Dashed lines are explained in text.

FIGURE 6. PARTIAL PRESSURES OF NaF FOR THE 19.2, 58.8, AND 73.9 MOLE PER CENT BeF_2 REGION

Values based on assumption that only NaF and BeF_2 exist in vapor phase. Solid lines are best curves through these data. Dashed lines are explained in text.

FIGURE 7. DATA FOR 15 MOLE PER CENT BeF₂ COMPOSITION

Interpretation of solid and dashed curves is the same as that given in Figures 4 and 5.

TABLE 3. VAPOR-PRESSURE DATA OF THE NaF-BeF₂ SYSTEM

Temperature, C	Observed pNaF, mm mercury	Observed pBeF ₂ , mm mercury	Flow Rate of Carrier Gas, cm ³ per min
<u>15.0 Mole Per Cent BeF₂</u>			
1061	1.082	0.43	40.1
1060	1.039	0.23	40.2
1043	0.742	0.29	40.0
1034	0.656	0.15	37.9
1023	0.563	0.22	37.3
1009	0.499	0.16	41.6
1008	0.485	0.13	35.7
993.8	0.345	0.092	39.3
991.4	0.353	0.14	39.3
985.2	0.314	0.14	51.4
978.7	0.277	0.082	49.4
961.8	0.229	0.066	47.4
961.8	0.189	0.078	49.5
960.4	0.169	0.074	52.8
942.6	0.140	0.040	50.1
939.0	0.128	0.044	51.3
938.9	0.130	0.026	50.9
929.9	0.112	0.029	45.4
917.3	0.0906	0.029	50.4
917.3	0.0797	0.029	49.2
903.8	0.0609	0.018	51.6
896.6	0.0567	0.018	50.7
887.0	0.0540	0.013	50.8
<u>19.2 Mole Per Cent BeF₂</u>			
1060	1.189	0.472	44.4
1051	1.018	0.334	39.8
1043	0.848	0.291	47.0
1026	0.619	0.205	47.1
1009	0.459	0.152	51.7
992.6	0.345	0.136	47.8
977.1	0.246	0.0640	50.6
961.4	0.208	0.0647	50.0
947.4	0.142	0.0404	51.2
931.6	0.0971	0.0278	50.2
917.6	0.0824	0.0227	50.2
903.3	0.0848	0.0168	49.8
896.4	0.0530	0.0148	49.6
890.7	0.0449	0.0142	51.4

TABLE 3. (Continued)

Temperature, C	Observed pNaF, mm mercury	Observed pBeF ₂ , mm mercury	Flow Rate of Carrier Gas, cm ³ per min
<u>24.5 Mole Per Cent BeF₂</u>			
1035	0.915	0.453	47.5
1025	0.736	0.467	49.9
1021	0.636	0.372	47.9
996.4	0.437	0.260	49.1
992.6	0.414	0.286	49.2
976.7	0.292	0.179	43.5
963.3	0.247	--	47.3
961.4	0.220	0.145	47.8
947.0	0.171	0.102	48.7
946.4	0.181	--	47.2
932.9	0.133	--	49.3
932.0	0.129	0.0755	48.9
926.7	0.114	0.0550	49.6
921.8	0.103	0.0438	51.3
916.7	0.0981	0.0527	48.8
910.0	0.0747	0.0356	47.2
909.5	0.0912	--	15.2
897.8	0.0620	0.0327	49.2
893.1	0.0607	0.0289	51.0
882.9	0.0486	0.0194	48.5
876.2	0.0431	--	48.9
867.1	0.0381	0.0202	48.4
856.8	0.0280	0.0128	50.8
836.0	0.0188	--	48.0
825.6	0.0125	0.00635	51.2
<u>31.5 Mole Per Cent BeF₂</u>			
1060	2.91	2.40	23.7
1060	2.41	2.19	22.6
1043	1.64	2.09	25.4
1043	1.67	1.99	25.7
1026	1.72	1.50	31.1
1026	1.30	1.72	25.1
1009	0.851	0.891	50.3
992.6	0.671	0.612	43.4
992.5	0.739	0.654	48.2
979.0	0.539	0.497	49.7
977.5	0.485	0.450	49.3
969.0	0.459	0.229	50.3
961.4	0.401	0.279	49.5
961.3	0.366	0.159	49.7
946.1	0.292	0.228	48.7
931.7	0.226	0.0667	48.2
931.6	0.224	0.190	53.8
917.5	0.165	0.117	51.0
916.9	0.160	0.0984	50.7

TABLE 3. (Continued)

Temperature, C	Observed pNaF, mm mercury	Observed pBeF ₂ , mm mercury	Flow Rate of Carrier Gas, cm ³ per min
<u>31.5 Mole Per Cent BeF₂ (Continued)</u>			
903.3	0.114	0.0577	49.2
903.3	0.115	0.0735	49.0
889.8	0.0907	0.0685	50.7
876.2	0.0689	0.0555	49.4
876.2	0.0698	0.0117	43.7
<u>39.5 Mole Per Cent BeF₂</u>			
1026	2.52	3.56	21.0
1010	2.05	3.35	21.8
994.2	1.52	2.28	21.5
978.5	1.15	1.99	21.9
961.4	0.950	1.34	26.5
946.9	0.672	1.02	33.5
917.3	0.399	0.616	47.3
896.3	0.257	0.409	48.5
876.2	0.166	0.240	49.0
855.4	0.113	0.189	48.1
<u>50.0 Mole Per Cent BeF₂</u>			
1012	3.35	16.0	19.5
996.8	2.73	14.1	16.3
987.0	2.70	13.6	14.2
983.2	2.20	12.3	15.4
975.6	1.82	8.53	44.6
970.7	2.01	9.68	13.4
961.4	1.61	8.85	15.4
956.6	1.23	6.57	29.8
932.0	0.952	5.71	24.2
918.3	0.677	3.89	30.4
916.1	0.727	3.71	18.9
895.3	0.450	2.72	26.8
877.9	0.312	1.90	34.1
854.4	0.191	1.27	41.0
833.5	0.130	0.804	47.5
815.1	0.0779	0.548	50.0
796.5	0.0547	0.367	49.7
<u>58.8 Mole Per Cent BeF₂</u>			
988.6	2.26	30.3	15.8
963.1	1.505	20.5	12.2
938.8	0.993	14.25	15.0
919.4	0.674	9.61	22.4
896.4	0.477	6.03	26.4
877.7	0.292	4.71	31.1
856.8	0.198	3.07	33.3
840.3	0.131	2.24	50.8

TABLE 3. (Continued)

Temperature, C	Observed pNaF, mm mercury	Observed pBeF ₂ , mm mercury	Flow Rate of Carrier Gas, cm ³ per min
<u>58.8 Mole Per Cent BeF₂ (Continued)</u>			
819.8	0.0855	1.43	50.5
802.2	0.0556	0.980	50.4
<u>73.9 Mole Per Cent BeF₂</u>			
976.9	1.36	48.5	13.7
956.0	0.851	37.2	13.9
937.0	0.684	23.6	19.7
910.3	0.372	15.0	21.9
890.2	0.248	10.1	22.3
871.0	0.170	7.67	26.5
850.4	0.108	4.63	30.2
833.4	0.0712	3.62	37.8
813.7	0.0512	2.32	37.2
800.6	0.0324	1.74	43.3
784.9	0.0234	1.18	50.3
768.5	0.0104	0.785	50.8
752.5	0.00817	0.482	50.6
736.8	0.00415	0.357	50.6
726.7	0.00422	0.288	49.4
717.9	0.00602	0.232	49.9
688.3	0.00158	0.110	50.0
670.2	0.00106	0.0635	49.8
657.4	0.00167	0.0483	49.4
635.7	--	0.0196	51.0
625.8	--	0.0101	50.2
604.0	--	0.00801	50.1
595.7	--	0.00526	50.4
574.3	--	0.00183	51.1
566.5	--	0.00192	51.0
539.8	--	0.000794	50.2
534.5	--	0.000823	51.0
514.3	--	0.00132	50.4
509.2	--	0.000555	50.6
490.2	--	< 0.000536	50.6
488.1	--	< 0.000564	50.2

FIGURE 8. PARTIAL PRESSURES OF NaF AND BeF₂ FOR NaF-BeF₂ SYSTEM AT 890 C ON THE BASIS THAT ONLY NaF AND BeF₂ EXIST IN VAPOR PHASE

FIGURE 9. PARTIAL PRESSURES AT 890 C ON THE BASIS THAT NaF, BeF₂, AND NaBeF₃ EXIST IN VAPOR PHASE

Construction of partial-pressure plots such as that shown in Figure 10 at 932 C indicates that this p' NaF peak becomes less prominent as the temperature is increased until finally it disappears. The explanation is postulated that the complex Na_2BeF_4 is rather unstable and dissociates readily into NaF and NaBeF_3 as the temperature is increased.

Having postulated that the vapor phase consists of Na_2BeF_4 in addition to NaF, BeF_2 , and NaBeF_3 , the next problem is the determination of the partial pressure of Na_2BeF_4 . The determination of p' NaBeF_3 was relatively simple because virtually all of the NaF was tied up in the complex NaBeF_3 ; therefore, the peak of the p'' NaF curve could be taken to be very nearly that of the p' NaBeF_3 curve. That the same simple situation does not exist for Na_2BeF_4 is evident from a study of Figure 9. The chief difficulty is that at 33-1/3 mpc* the three molecular species which contain sodium atoms, NaF, NaBeF_3 , and Na_2BeF_4 , appear to exert vapor pressures having the same order of magnitude. It is clear that in order to solve the problem other helpful relations have to be called upon. In the vapor phase we have these basic reactions:

From these, the following equilibrium constants are obtained:

$$K_1 = \frac{(p\text{NaF})(p\text{BeF}_2)}{(p\text{NaBeF}_3)} \quad (9)$$

$$K_2 = \frac{(p\text{NaF})(p\text{NaBeF}_3)}{(p\text{Na}_2\text{BeF}_4)} \quad (10)$$

$$K_3 = \frac{K_1}{K_2} = \frac{(p\text{BeF}_2)(p\text{Na}_2\text{BeF}_4)}{(p\text{NaBeF}_3)^2} \quad (11)$$

Only two of these equilibrium constants are, of course, independent.

Results obtained with the transpiration apparatus are based only on the number of moles of NaF and BeF_2 present in the condenser without regard to complexes formed. The resulting equations are:

$$N_{\text{NaF}} = n\text{NaF} + n\text{NaBeF}_3 + 2n\text{Na}_2\text{BeF}_4 \quad (12)$$

$$N_{\text{BeF}_2} = n\text{BeF}_2 + n\text{NaBeF}_3 + n\text{Na}_2\text{BeF}_4 \quad (13)$$

where N_{NaF} and N_{BeF_2} are the moles of NaF and BeF_2 , respectively, in the condenser regardless of complexes formed, and n represents the moles of the particular molecular species. Since $p \propto n$ for partial pressures of the order of 10 mm mercury or less**, we have

*Because of its frequency of occurrence, the phrase "mole per cent BeF_2 composition" has been abbreviated to "mpc".

**See Appendix of Reference (1).

FIGURE 10. PARTIAL PRESSURES AT 932 C ON THE BASIS THAT NaF, BeF₂, AND NaBeF₃ EXIST IN VAPOR PHASE

$$p''\text{NaF} = p\text{NaF} + p\text{NaBeF}_3 + 2p\text{Na}_2\text{BeF}_4 \quad (14)$$

$$p''\text{BeF}_2 = p\text{BeF}_2 + p\text{NaBeF}_3 + p\text{Na}_2\text{BeF}_4 \quad (15)$$

Another helpful relation would be

$$\text{Total pressure} = p\text{NaF} + p\text{BeF}_2 + p\text{NaBeF}_3 + p\text{Na}_2\text{BeF}_4 \quad (16)$$

For sufficiently low pressures, Equations (14), (15), and (16) could be used simultaneously. It must be pointed out, however, that (16) would be of little value where one or two components exert a much larger vapor pressure than do the other components. In any event, for Equation (16) to be of any value, the total pressure would have to be determined very accurately.

Since no direct experimental information was available on either the total pressure of the system or the equilibrium constants, only two equations remained, with four unknowns. Hence, the system could not be solved explicitly in terms of the partial pressures of the various components. However, rather than leave the system indeterminate, efforts were made to obtain an approximate solution by reasonable estimates and successive approximations.

Estimation of Partial Pressures by Approximation Methods

An analysis of the partial pressures of the various vapor-phase components was limited to the 890 to 1050 C range since this was the limit of the temperature range over which data were available for almost all compositions of the difficult NaF-rich region. The first step in resolving this region was to approximate, from available information, the partial pressures of NaF as a function of temperature for the 15.0, 19.2, 24.5, and 31.5 mpc's. It was indicated above that, for a vapor phase assumed to consist only of NaF, BeF₂, and NaBeF₃, the p'NaF peak which is evident in Figure 9 disappears in pressure-composition plots constructed at higher temperatures. The interpretation was that Na₂BeF₄ is unstable and dissociates readily into NaF and NaBeF₃. Hence, for high-temperature pressure-composition plots the p'NaF and pNaF curves should be nearly coincidental in the NaF-rich region. Using this result, the pNaF's were estimated for the 15.0, 19.2, 24.5, and 31.5 mpc's at 1017 C. The NaF-BeF₂ phase diagrams by Thilo and Schröder⁽³⁾ aided in the determination of pNaF for 15 mpc at 890 C, the lower limit of the temperature range. According to that diagram the melting point of this particular composition is very nearly 890 C. By use of Equation (4), pNaF at this composition and temperature was calculated to be 0.036 mm of mercury. The slopes of the log pNaF vs. $\frac{1}{T}$ curve for 15 mpc and for pure liquid NaF turned out to be nearly the same. It was then assumed that the slopes of the log pNaF vs. $\frac{1}{T}$ curves were nearly the same for the 0 to 31.5 mpc region. This result used together with the pNaF estimates for various compositions at 1017 C gave pNaF estimates for compositions at 890 C. Having obtained this estimate, the number of unknowns for Equations (14) and (15) was reduced from 4 to 3 for the 15.0, 19.2, 24.5, and 31.5 mpc's.

The partial pressures $p\text{NaBeF}_3$, $p\text{BeF}_2$, and $p\text{Na}_2\text{BeF}_4$ were then estimated for the various compositions and temperatures in such a manner that (a) the resulting $\log p''$ vs. $\frac{1}{T}$ curves provided the best fit through the experimental points given in Figures 4, 5, 6, and 7 and (b) the $\log K_p$ vs. $\frac{1}{T}$ curves obtained from these partial pressures yielded reasonable ΔS° values for the Reactions (7) and (8). Condition (a) was not easy to satisfy because the scatter of the experimental points for some compositions was such that it was difficult to decide on the best curve through these points. The estimated partial pressures which seemed to satisfy Condition (a) were then used to calculate the equilibrium constants given in Equations (9) and (10) for the various compositions and temperatures. The logarithms of the equilibrium constants, K_{ip} , were then plotted as functions of $\frac{1}{T}$ and the best straight lines drawn through these points. From these plots equations of the type

$$\log K_p = A + \frac{B}{T} \quad (17)$$

were obtained for Reactions (7) and (8). By means of relations

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (18)^*$$

and

$$\Delta F^\circ = -RT \ln K_p \quad (19)$$

Values of ΔS° values were obtained for these reactions by substitution in the equation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} \quad (20)^*$$

To satisfy Condition (b), the $\log K_p$ vs. $\frac{1}{T}$ curves were so adjusted as to yield reasonable ΔS° values while still satisfying Condition (a). The extent to which Condition (a) was satisfied is apparent from the fit of the dashed curves with the experimental points given in Figures 4, 5, 6, and 7. The poorest fit is manifestly that of $p''\text{BeF}_2$ for 15.0 mpc (Figure 7). However, an effort to correct this situation led to other changes which resulted in a less satisfactory over-all solution. It is interesting to observe that, in general, the best fit was obtained for those compositions whose experimental values showed the least scatter.

The efforts to satisfy Condition (b) and Condition (a) simultaneously produced these results:

For the reaction

* ΔH° may be replaced by ΔH , since at moderate pressures $\Delta H^\circ \approx \Delta H$.

there was obtained

$$\log K_1p = 6.67 - \frac{14.66 \times 10^3}{T(K)} \quad (21)$$

$$\Delta H = 67.1 \text{ kcal per g-mole} \quad (22)$$

$$\Delta S_{1300K}^0 = 30.5 \text{ e.u.} \quad (23)$$

For the reaction

there resulted

$$\log K_2p = 14.11 - \frac{21.89 \times 10^3}{T(K)} \quad (24)$$

$$\Delta H = 100 \text{ kcal per g-mole} , \quad (25)$$

$$\Delta S_{1300K}^0 = 64.6 \text{ e.u.} \quad (26)$$

The ΔS^0 value for Reaction (7) seems to be reasonable. The fact that ΔS^0 is rather high for Reaction (8) is due in part to the large ΔH value. This large ΔH value is the result of the rather rapid dissociation of Na_2BeF_4 as the temperature is increased. This is the type of behavior that might be expected, for while NaBeF_3 should form rather stable tetrahedral bonding, no such stable bonding is evident for Na_2BeF_4 .

The discussion so far has led to the determination of $\log p$ vs. $\frac{1}{T}$ curves for the 15.0, 19.2, 24.5, and 31.5 mpc's as well as Kp-T Equations (21) and (24), which hold for the entire NaF-BeF₂ system. By using Equations (21) and (24), it was then not difficult to determine the $\log p$ vs. $\frac{1}{T}$ curves of the various components for the 39.5, 50.0, 58.8, and 73.9 mpc's. Since for these compositions

$$p\text{NaF} < p\text{Na}_2\text{BeF}_4 << p\text{NaBeF}_3 \quad (27)$$

$$p\text{Na}_2\text{BeF}_4 << p\text{BeF}_2 , \quad (28)$$

there resulted

$$p\text{NaBeF}_3 \approx p'\text{NaBeF}_3 \quad (29)$$

$$p\text{BeF}_2 \approx p'\text{BeF}_2 . \quad (30)$$

Hence, the partial pressures of the various components could be obtained for these compositions by repeated applications of Equations (9), (10), and (11), together with Equations (14) and (15).

Thus a set of partial pressures was derived over 890 to 1050 C for the NaF-BeF₂ system which was self-consistent with the equilibrium constants given in Equation (9) and (10) simultaneously, the logarithms of the partial pressures and the equilibrium constants varying smoothly and linearly with $\frac{1}{T}$ in that temperature range.

Figures 11 and 12 show how the partial pressures of the vapor-phase components vary with composition for two temperatures. These plots bear a superficial resemblance to the usual liquid-solid phase diagrams in that the location of the peak of a curve indicates the presence of a complex and gives its composition. A tabulation of all the derived constants of the partial-pressure equations for NaF, BeF_2 , NaBeF_3 , and Na_2BeF_4 is given in Table 4.

Recent findings by Miller and Kusch⁽⁴⁾ show the gaseous phase to be even more complex. From a measurement of the velocity distribution of molecules in a beam produced by NaF vapor effusing through a small slit, they were able to determine the concentration of dimers and trimers in the NaF vapor phase. Results obtained by them over the 842 to 916 C temperature range indicated a concentration of polymers in the vapor phase sufficiently great to lower the results obtained from the transpiration method by about 10 per cent. However, since their findings showed the concentration of dimers and trimers to be temperature dependent, and since the upper temperature limit of Battelle's studies extended some 130 C beyond theirs, no vapor-pressure corrections were made for NaF. In any event, if data on dimers and trimers were available over this temperature range, the resulting changes would be expected to be relatively minor.

Derived Phase Diagram

Using the results given in Table 4, a phase diagram, Figure 13, was constructed for the NaF- BeF_2 system at a pressure of 1 mm of mercury. The composition of the azeotrope was found to be pressure dependent. The peculiar-looking indentation of the vapor-composition curve is quite real. It stems from the fact that the complex NaBeF_3 exerts an appreciable partial pressure. This dip occurs even when the construction of this phase diagram is based on the assumption that only NaF and BeF_2 molecules exist in the vapor phase. Hence, the presence of a dip in the vapor-composition curve indicates the existence of a molecular complex in the vapor phase. The prominence of this dip bears a relationship to the vapor pressure of this complex. Of course, if the other components exert vanishingly small partial pressures at the composition indicated by the partial-pressure peak of the complex, the vapor phase would have the same composition as the liquid phase, and the liquid- and vapor-composition curves would meet.

Total Vapor Pressures of the NaF- BeF_2 System

Figure 14 shows how the total pressure of the NaF- BeF_2 system varies with composition for two temperatures. The behavior of the lower temperature vapor-pressure curve in the high-NaF-composition region is explained by the fact that the solid NaF phase is present over the 0 to 15 mpc range (see Figure 11). While pNaF remains constant over that composition region, the other partial pressures increase as the composition becomes richer in BeF_2 . Beyond 15 mpc, the liquid phase begins and the pNaF starts to drop. Since pNaF is greater at that point than the sum of the other partial pressures, the total pressure decreases until about 19 mpc is reached. From that point on the other partial pressures predominate, resulting in an increase in the total vapor pressure.

FIGURE 11. PARTIAL PRESSURES AT 890°C ON THE BASIS THAT NaF , BeF_2 , NaBeF_3 , AND Na_2BeF_4 EXIST IN VAPOR PHASE

FIGURE 12. PARTIAL PRESSURES AT 1017 C ON THE BASIS THAT NaF, BeF₂, NaBeF₃, AND Na₂BeF₄ EXIST IN VAPOR PHASE

TABLE 4. DERIVED VAPOR-PRESSURE CONSTANTS FOR THE NaF-BeF₂ SYSTEM ON THE BASIS THAT THE VAPOR PHASE IS COMPOSED OF NaF, BeF₂, NaBeF₃, AND Na₂BeF₄

$$\log p = A - \frac{B \times 10^3}{T(K)}$$

Composition, mole per cent BeF ₂	p BeF ₂		p NaF		p NaBeF ₃		p Na ₂ BeF ₄	
	A	B	A	B	A	B	A	B
73.9	10.507	11.047	8.81	15.68	9.771	12.064	1.593	5.848
58.8	10.024	10.810	9.36	15.78	9.843	11.938	2.286	5.918
50.0	9.536	10.726	10.04	16.07	9.903	11.977	3.084	6.320
39.5	8.916	11.353	10.56	15.68	9.942	12.391	3.513	6.183
31.5	12.35	17.01	8.93	12.89	11.702	15.208	3.651	6.221
24.5	12.31	18.06	9.077	12.598	11.930	16.095	3.985	6.769
19.2	12.76	19.29	9.126	12.426	12.33	17.04	4.517	7.637
15.0	13.18	20.32	9.212	12.391	12.82	18.01	5.04	8.51

FIGURE 13. PHASE DIAGRAM FOR THE NaF-BeF₂ SYSTEM AT A PRESSURE OF 1 MM MERCURY

FIGURE 14. TOTAL VAPOR PRESSURE OF NaF-BeF_2 SYSTEM AT 890 C AND 1017 C ON THE BASIS THAT NaF , BeF_2 , AND Na_2BeF_4 EXIST IN VAPOR PHASE

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