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VAPOR PRESSURES OF THE RUBIDIUM FLUORIDE-ZIRCONIUM FLUORIDE
AND LITHIUM FLUORIDE-ZIRCONIUM FLUORIDE SYSTEMS

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The vapor pressures of RbF and LiF were measured over the temperature intervals 589 to 1059 C and 851 to 1060 C, respectively. Thermal analysis showed the melting point of RbF to be 798 C. Vapor pressures of the RbF-ZrF₄ and LiF-ZrF₄ systems were measured over the ranges 690 to 1060 C and 670 to 1060 C, respectively. On the basis of previously developed theory, it was concluded that the complexes, RbZr₂F₉ and LiZr₂F₉ exist in the vapor phase of the respective systems. Further work on the NaF-ZrF₄ system points to the existence of the gaseous complex NaZr₂F₉ rather than NaZrF₅ as previously supposed. A phase diagram derived from the vapor-pressure data was constructed for the RbF-ZrF₄ system at a total pressure of 1 mm of mercury. This diagram shows a constant boiling point to exist in the vicinity of 33-1/3 mole per cent ZrF₄. Melting-point curves are presented for the various systems.

INTRODUCTION

This is a further report on the physical properties of fused-salt systems. Previous work has dealt with the NaF-ZrF₄⁽¹⁾ and NaF-BeF₂ systems⁽²⁾. The present study is concerned with the RbF-ZrF₄ and LiF-ZrF₄ systems.

EXPERIMENTAL PROCEDURE

Description of Method and Apparatus

The method and apparatus used have been described previously.^(1,2,3) No changes were made in undertaking the present study.

Materials

The pure salts and all fused-salt mixtures were supplied by the Oak Ridge National Laboratory at Oak Ridge, Tennessee.

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

RESULTS

The Vapor Pressure of RbF

The results of the measurements on RbF are given in Table 1. The melting point of RbF could not be determined with any certainty from a plot of these data alone. Hence, the melting point, 798 C, was obtained by thermal analysis. This value, which fits in quite well with the vapor-pressure data, is about 23 C higher than that given by Brewer⁽⁴⁾. At 912 C, a vapor pressure of 4.9 mm of mercury was calculated. This value is about 6.5 times greater than that given by Brewer.

The P-T relationships for solid RbF were expressed by an equation of the type $\log p = A + \frac{B}{T}$. For liquid RbF this was not possible, since a curvature was evident when the logarithms of the pressures were plotted as a function of the reciprocal temperatures. Hence, for liquid RbF, the P-T relationship was expressed in the form $\log p = A + \frac{B}{T} + C \log T$. The results are as follows:

From 798 to 1059 C:

$$\log P \text{ mm Hg} = 63.823 - \frac{17772}{T(K)} - 15.660 \log T(K) \quad (1)$$

From 589 to 798 C:

$$\log P \text{ mm Hg} = 10.263 - \frac{11226}{T(K)} \quad (2)$$

Melting point:

$$798 \text{ C} \quad (3)$$

The Vapor Pressure of LiF

The vapor-pressure data obtained for LiF are given in Table 2. A least-squares treatment gave these results for the 851 to 1060 C range:

$$\log P \text{ mm Hg} = 8.797 - \frac{11409}{T(K)} \quad (4)$$

$$\Delta H \text{ vaporization} = 52.2 \text{ k cal per g-mole} \quad (5)$$

For 908 C, a vapor pressure of 0.14 mm of mercury is calculated from Equation (4). This value is almost twice as great as that given by Brewer⁽⁴⁾.

The lowest temperature for which data are given in Table 2 is 850.6 C. Actually, runs were made below this temperature. However, since the scatter increased greatly below that temperature, these data were not included in the least-squares treatment. For comparison purposes they are plotted later in the report in Figure 9.

TABLE 1. VAPOR PRESSURES OF RbF

Temperature, C	Vapor Pressure, mm of mercury		Deviation, per cent	Flow Rate of Carrier Gas, cm ³ per min
	Observed	Calculated		
1059	35.3	35.5	-0.6	19.3
1041	29.1	28.7	+1.4	21.0
1024	23.1	23.5	-1.7	20.5
1002	17.4	17.8	-2.2	20.2
975.5	12.8	12.6	+1.6	19.7
944.8	8.04	8.12	-1.0	24.2
916.0	5.27	5.24	+0.6	29.0
884.1	3.09	3.10	-0.3	36.4
863.4	2.16	2.18	-0.9	43.7
837.9	1.37	1.35	+1.5	50.6
814.2	0.833	0.848	-1.8	50.2
790.3	0.513	0.509	+0.8	50.4
768.9	0.308	0.309	-0.3	49.2
747.2	0.186	0.182	+2.2	51.0
727.1	0.105	0.109	-3.7	49.9
707.1	0.0669	0.0647	+3.4	51.9
686.7	0.0346	0.0370	-6.5	48.9
670.2	0.0242	0.0230	+5.2	50.6
635.3	0.00756	0.00805	-6.1	49.1
619.5	0.00524	0.00487	+7.6	50.8
603.9	0.00280	0.00291	-3.8	49.3
588.9	0.00188	0.00174	+8.0	50.9

TABLE 2. VAPOR PRESSURES OF LiF

Temperature, C	Vapor Pressure, mm of mercury		Deviation, per cent	Flow Rate of Carrier Gas, cm ³ per min
	Observed	Calculated		
1060	1.56	1.74	-10.3	49.0
1044	1.24	1.36	-8.8	49.9
1043	1.22	1.34	-9.0	9.8
1034	1.35	1.17	+15.4	48.1
1026	0.900	1.03	-12.6	49.5
1009	0.759	0.794	-4.4	49.8
1009	0.796	0.788	+1.0	49.9
992.6	0.669	0.608	+10.0	40.6
992.5	0.724	0.607	+19.3	49.9
992.4	0.684	0.606	+12.9	50.5
977.2	0.462	0.471	-1.9	49.4
977.0	0.486	0.469	+3.6	49.3
961.1	0.366	0.358	+2.2	50.6
946.3	0.249	0.277	-10.1	61.4
939.0	0.260	0.243	+7.0	49.9
930.9	0.240	0.210	+14.3	57.5
921.7	0.170	0.178	-4.5	50.8
903.3	0.131	0.126	+4.0	49.5
890.7	0.0921	0.0988	-6.8	48.9
878.5	0.0735	0.0778	-5.5	49.0
863.2	0.0498	0.0572	-12.9	50.3
850.6	0.0473	0.0442	+7.0	51.5

The Vapor Pressures of the RbF-ZrF₄ System

Discussion of the Data Obtained

The vapor-pressure data obtained for the RbF-ZrF₄ system are given in Table 3 and plotted in Figures 1 through 4. The p' ZrF₄* data for 15 mpc** were not plotted because of overlap with the p' ZrF₄ data for 24.5 mpc. As in previous reports, these data were listed on the basis that only the simplest molecular species, in this case RbF and ZrF₄, exist in the vapor phase. Inspection of Table 3 shows that some data are missing for ZrF₄ at 15 mpc. Much difficulty was experienced in obtaining consistent data for ZrF₄ for this composition. In order to resolve the difficulty, much longer runs were made so that more material could be collected in the condenser. In addition, the condenser was washed out even more thoroughly for the runs for which ZrF₄ data are given. For 15 mpc, all results are listed from runs where the condenser was given a minimum of 13 washes of 1/2-hr each. In some cases the condenser was given as many as nineteen 1/2-hr washes. The same situation held for the results obtained for 24.5 mpc. For this particular composition, the scatter is very large below 880 C. Why this is so is not clear.

Molecular Composition of the Vapor Phase

A pressure-composition plot for 890 C is shown in Figure 5. The vertical lines through these and other curves represent qualitatively the degree of uncertainty of the data obtained. The circles represent the best values. It is noted that the partial pressure of RbF goes through a maximum.

From theory developed in a previous report⁽¹⁾, this peak is evidence for the existence of a molecular complex in the vapor phase. According to the Duhem-Margules equation,

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

the composition of the complex is given by the peak of the partial-pressure curve. Examination of the curve shows the peak to exist between 50 and 75 mpc. The simplest complex which can be postulated to exist, consists, therefore, of one molecule of RbF and two molecules of ZrF₄. This leads to a molecule having the composition RbZr₂F₉, and means that the partial-pressure peak must occur at 66.7 mpc. It is quite evident from an examination of the plot that this latter condition is fulfilled. In accordance with the procedure outlined previously⁽¹⁾, the partial pressures of the various components were calculated for various temperatures. Figure 6 shows the results of these calculations for 890 C. Table 4 lists the constants of the P-T equations for the various components.

*For simplicity, partial pressures calculated on the basis that only RbF (LiF) and ZrF₄ exist in the vapor phase will be denoted by a prime; partial pressures calculated on the basis that RbZr₂F₉ (LiZr₂F₉) exists in the vapor phase, in addition to RbF (LiF) and ZrF₄, will be given without any primes.

**Abbreviation for the phrase "mole per cent ZrF₄ composition".

TABLE 3. VAPOR-PRESSURE DATA OF THE RbF-ZrF₄ SYSTEM

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pRbF	pZrF ₄	
<u>72.9 Mole Per Cent ZrF₄</u>			
876.2	0.793	210	5.2
862.7	0.822	177	6.5
850.4	0.507	142	7.9
838.1	0.341	113	8.0
825.8	0.283	92.8	11.7
814.0	0.180	79.2	12.1
802.1	0.205	61.7	14.7
790.7	0.119	48.0	16.5
779.2	0.145	37.4	17.1
768.5	0.0976	32.3	18.1
752.5	0.0574	21.0	17.3
737.2	0.0473	14.1	14.7
727.0	0.0362	10.1	21.6
716.9	0.0242	7.69	23.9
707.2	0.0275	5.37	26.5
698.6	0.0198	4.65	33.3
<u>65.2 Mole Per Cent ZrF₄</u>			
969.3	4.33	224	5.5
946.8	3.60	182.4	5.0
916.4	2.17	119	8.0
890.3	1.48	85.8	10.3
861.6	0.682	52.5	13.0
837.7	0.613	36.3	14.9
815.3	0.340	25.5	15.6
790.4	0.152	16.8	14.7
770.2	0.144	10.9	20.4
745.4	0.0940	6.19	24.2
<u>55.8 Mole Per Cent ZrF₄</u>			
1026	11.0	200	4.3
1008	7.61	153.2	6.0
993	5.01	141.1	5.3
977.1	4.58	110.3	5.1
944.9	3.46	71.4	10.7
917.9	1.75	49.4	15.5
888.0	1.09	31.6	15.3
864.2	0.697	21.3	15.4
837.0	0.359	13.0	15.7
836.6	0.455	14.2	20.4

TABLE 3. (Continued)

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pRbF	pZrF ₄	
<u>55.8 Mole Per Cent ZrF₄</u> (Continued)			
815.2	0.260	9.43	21.5
790.2	0.135	6.16	25.3
770.2	0.112	3.98	25.4
746.3	0.0581	2.62	25.2
738.8	0.0450	2.17	27.7
728.8	0.0349	1.72	30.8
715.1	0.0306	1.27	49.5
706.5	0.0275	1.10	48.4
696.7	0.0141	0.900	49.2
690.1	0.0112	0.685	50.9
<u>49.0 Mole Per Cent ZrF₄</u>			
1009	7.10	71.2	7.6
991.3	4.90	54.8	9.2
976.9	3.75	46.6	14.8
976.7	3.64	47.8	13.4
946.8	2.72	24.3	15.9
917.1	1.65	21.3	17.8
903.8	1.10	16.6	18.0
889.5	1.09	13.5	20.7
876.8	0.684	9.56	21.7
863.4	0.433	8.92	23.0
851.5	0.418	6.86	24.6
838.1	0.294	5.82	25.6
812.8	0.193	3.87	28.8
790.9	0.121	2.43	30.7
781.2	0.0819	2.00	32.3
767.9	0.0574	1.67	34.4
756.0	0.0457	1.19	36.3
747.6	0.0650	1.05	40.8
738.7	0.0364	0.821	45.5
726.9	0.0281	0.689	49.7
716.4	0.0221	0.497	50.2
<u>39.5 Mole Per Cent ZrF₄</u>			
1060	5.71	10.5	8.4
1043	4.25	7.60	10.3
1025	3.22	5.87	12.0
1005	2.31	4.93	15.1

TABLE 3. (Continued)

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pRbF	pZrF ₄	
<u>39.5 Mole Per Cent ZrF₄</u> (Continued)			
984.7	1.59	3.38	20.7
976.6	1.50	2.55	25.8
954.4	0.992	2.22	25.3
946.4	0.889	1.78	26.7
931.6	0.636	1.36	29.9
917.7	0.506	1.13	33.0
889.4	0.289	0.701	39.3
876.2	0.222	0.542	37.1
864.0	0.178	0.441	49.0
850.4	0.132	0.351	49.4
838.0	0.105	0.260	49.7
825.7	0.0840	0.207	50.6
<u>24.5 Mole Per Cent ZrF₄</u>			
1043	9.54	--	10.2
1034	8.44	0.20	11.1
1026	8.14	--	10.8
1017	6.47	0.33	15.7
1009	6.23	--	17.5
1002	5.73	0.187	17.5
993	5.15	--	20.2
984.8	4.10	0.156	24.7
976.6	4.15	--	26.8
961.3	3.22	--	26.8
953.4	2.75	0.062	28.9
946.3	2.51	--	35.4
931.5	1.96	0.070	36.3
916.8	1.53	--	40.2
904.6	1.104	0.011	35.6
889.7	1.05	0.0088	46.1
889.4	1.01	--	41.1
880.5	0.804	0.0216	41.3
870.7	0.746	0.094	47.1
863.3	0.700	0.0022	50.7
856.6	0.642	0.047	48.2
850.7	0.627	0.011	50.6
850.6	0.617	0.00028	51.0
846.7	0.557	0.0011	50.4
838.9	0.607	0.054	49.2
838.2	0.575	0.00065	49.2
825.7	0.532	0.048	49.0

TABLE 3. (Continued)

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pRbF	pZrF ₄	
<u>24.5 Mole Per Cent ZrF₄</u>			
(Continued)			
813.6	0.492	0.0034	47.7
807.3	0.461	0.050	48.9
796.2	0.362	0.033	49.9
790.5	0.307	0.042	49.7
779.4	0.284	0.0020	49.9
<u>15.0 Mole Per Cent ZrF₄</u>			
1060	21.9	--	10.3
1060	25.6	0.94	11.9
1043	19.1	--	7.9
1043	20.5	0.13	10.7
1026	14.6	0.46	12.1
1009	13.0	0.12	22.5
1002	9.55	0.23	16.0
993	10.1	0.063	16.3
976.7	7.42	--	14.2
961.5	6.74	0.27	19.8
961.4	6.47	0.058	19.7
946.2	5.09	--	21.4
931.9	3.51	0.17	25.1
931.6	4.49	0.14	32.5
917.1	3.16	--	28.8
902.8	2.79	0.049	37.5
902.7	2.80	0.012	32.3
888.0	1.96	--	39.3
876.2	1.68	0.044	46.2
876.1	1.55	0.062	39.9
863.3	1.33	--	39.3
863.2	1.43	0.048	31.2
850.4	1.27	0.0081	50.5
839.5	0.881	--	48.8
832.4	0.796	0.0045	50.2
832.1	0.671	0.033	49.9
814.3	0.525	--	47.4
789.8	0.325	--	49.6
769.0	0.216	--	49.7
757.2	0.175	--	49.7
747.1	0.146	--	50.7

FIGURE 1. PARTIAL PRESSURES OF ZrF_4 OF RbF-ZrF_4 SYSTEM ON THE BASIS THAT ONLY RbF AND ZrF_4 EXIST IN THE VAPOR PHASE

Figures on plot denote mole per cent ZrF_4 composition.

FIGURE 2. VAPOR PRESSURE OF RbF AND PARTIAL PRESSURES OF RbF FOR 15 AND 24.5 MOLE PER CENT ZrF₄ COMPOSITIONS OF RbF-ZrF₄ SYSTEM ON THE BASIS THAT ONLY RbF AND ZrF₄ EXIST IN THE VAPOR PHASE

FIGURE 3. PARTIAL PRESSURES OF RbF FOR 39.5, 49.0, AND 55.8 MOLE PER CENT ZrF₄ COMPOSITIONS OF RbF-ZrF₄ SYSTEM ON THE BASIS THAT ONLY RbF AND ZrF₄ EXIST IN THE VAPOR PHASE

FIGURE 4. PARTIAL PRESSURES OF RbF FOR 65.2 AND 72.9 MOLE PER CENT ZrF₄ COMPOSITIONS OF RbF-ZrF₄ SYSTEM ON THE BASIS THAT ONLY RbF AND ZrF₄ EXIST IN THE VAPOR PHASE

FIGURE 5. PARTIAL PRESSURES OF RbF- ZrF_4 SYSTEM AT 890 C ON THE BASIS THAT ONLY RbF AND ZrF_4 EXIST IN THE VAPOR PHASE

FIGURE 6. PARTIAL PRESSURES OF RbF-ZrF₄ SYSTEM AT 890 C

Because of the steepness of the slopes of the partial pressure curves the equilibrium constant, K_p , was not calculated for the reaction,

TABLE 4. DERIVED VAPOR-PRESSURE CONSTANTS FOR THE RbF-ZrF₄ SYSTEM ON THE BASIS THAT THE VAPOR PHASE IS COMPOSED OF RbF, ZrF₄, AND RbZr₂F₉

$$\text{Log } P \text{ mm Hg} = A - \frac{B \times 10^3}{T(K)} - C \log T(K)$$

Composition, mole per cent ZrF ₄	pRbZr ₂ F ₉		pZrF ₄		pRbF		
	A	B	A	B	A	B	C
72.9	9.424	10.925	10.374	9.248	--	--	--
65.2	9.504	10.897	9.665	9.024	--	--	--
55.8	9.534	11.025	9.178	8.970	--	--	--
49.0	9.418	11.052	8.766	8.975	--	--	--
39.5	8.898	10.995	5.7	7.7	--	--	--
24.5	7.723	11.178	--	--	53.988	16.894	12.877
15	--	--	--	--	57.133	16.818	13.815

Figure 7 is a phase diagram of the RbF-ZrF₄ system for a pressure of 1 mm of mercury constructed from the values given in Table 4. An azeotrope is evident which seems to have a composition corresponding to 2 moles of RbF and 1 mole of ZrF₄. Not enough work has been done to determine whether or not the composition of this azeotrope is pressure dependent.

Melting Points

From Figure 1 the melting point for 72.9 mpc is determined to be 760 C. The melting point for 24.5 mpc is a few degrees higher than that indicated in Figure 2. The reason is that the data plotted represent the total RbF present. From this total, the RbF which is tied up as RbZr₂F₉ must be subtracted. Thermal analysis established the melting point to be 877 C for 24.5 mpc. Below the melting point, the pRbF curve breaks the way it does because the composition of the melt shifts toward RbF. This is quite evident from Figure 6. At $\frac{1}{T(K)} = 9.33 \times 10^{-4}$ (799 C), the pRbF curves for 15 mpc and 24.5 mpc join. This means that the melting point for 15 mpc is 799 C.

FIGURE 7. PHASE DIAGRAM FOR THE $RbF-ZrF_4$ SYSTEM AT A PRESSURE OF 1 MM OF MERCURY

The Vapor Pressures of the LiF-ZrF₄ System

Molecular Composition of the Vapor Phase

The vapor-pressure data for the LiF-ZrF₄ system are given in Table 5 and plotted in Figures 8 through 13. The peculiar shape of the 82 mpc curve in Figure 13 is not apparent from the data, and will be explained later. Again, these are the raw data without regard to complexes present in the vapor phase. A pressure-composition plot for 890 C is given in Figure 14. Just as pRbF exhibited a partial-pressure peak in the RbF-ZrF₄ system, so pLiF exhibits a partial-pressure peak in the LiF-ZrF₄ system. It is clear that the peak must occur between 60 and 82 mpc. The simplest complexes in this region are LiF·2ZrF₄ and LiF·3ZrF₄, corresponding to a pLiF peak at 66.7 and 75 mpc, respectively. That the peak occurs at 75 mpc is unlikely, since this would result in a very abrupt partial-pressure drop from 75 to 82 mpc. Since a pLiF peak at 66.7 mpc seems much more reasonable, the curve was constructed as having its peak at that composition. Partial pressures of the various components, LiF, LiZr₂F₉, and ZrF₄, were calculated as previously outlined.⁽¹⁾ Figure 15 shows the results of these calculations for 890 C. Table 6 lists the constants of the P-T equations for the various components. Because the partial pressures of all three components were not known with any certainty for any one composition, no attempt was made to obtain an equilibrium constant, K_p, for the reaction:

A phase diagram was not constructed for the LiF-ZrF₄ system. However, from an inspection of Figure 15 it does not appear that an azeotrope exists for a total pressure of about 0.1 mm of mercury.

Melting Points

Figure 8 shows the melting point for 61.8 mpc to be 724 C. For 82 mpc, it is approximated as being 865 C. The peculiar shape of the pLiZr₂F₉ (identical with pLiF) curve for 82 mpc is explained as follows. Below 865 C ($\frac{1}{T(\text{K})} = 8.79 \times 10^{-4}$), the solid ZrF₄ phase starts to separate out. This means, of course, that the composition of the liquid shifts toward LiF. Figure 15 shows that pLiZr₂F₉ increases sharply from 82 to 66.7 mpc. Hence, the 82 mpc curve in Figure 13 increases and attains a maximum vertical displacement from the 61.8 curve at $\frac{1}{T(\text{K})} = 9.57 \times 10^{-4}$, since this is the temperature at which the melt has the composition 66.7 mpc. Below this temperature, the melt becomes still richer in LiF, but pLiZr₂F₉ drops also (see Figure 15). Hence, the 82 mpc curve approaches the 61.8 mpc curve until they finally join at $\frac{1}{T(\text{K})} = 10.03 \times 10^{-4}$. Since this is the melting point for 61.8 mpc, the pLiZr₂F₉ curve for 61.8 mpc breaks slightly at this temperature.

Figure 16 shows melting-point curves for the systems LiF-ZrF₄ and RbF-ZrF₄, as well as NaF-ZrF₄.⁽¹⁾

TABLE 5. VAPOR-PRESSURE DATA FOR THE LiF-ZrF₄ SYSTEM

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pLiF	pZrF ₄	
<u>82 Mole Per Cent ZrF₄</u>			
890.3	0.085	499	3.8
885.5	0.097	468	4.0
881.1	0.10	451	4.8
876.5	0.058	391	4.0
869.7	0.069	352	4.6
850.4	0.076	240	7.2
841.9	0.134	187	6.9
825.5	0.0315	129	11.1
814.5	0.078	102.7	6.8
802.1	0.0345	73.8	13.9
781.6	0.024	44.7	15.8
757.7	0.0147	23.5	8.0
757.7	0.0074	26.2	13.8
737.2	0.0068	12.9	20.9
717.0	0.0035	7.70	26.4
716.9	0.0041	7.41	23.4
<u>61.8 Mole Per Cent ZrF₄</u>			
892.4	0.357	191	5.6
889.5	0.236	198	4.6
869.7	0.318	131	6.5
865.4	0.287	136	4.4
863.3	0.257	131	5.0
847.1	0.0924	98.9	6.5
837.4	0.139	85.3	5.6
825.7	0.0745	63.4	5.5
813.9	0.0631	57.7	15.8
779.7	0.0195	25.5	10.4
779.3	0.0285	29.3	20.5
765.2	0.0162	22.5	24.1
751.3	0.0145	16.0	25.8
737.9	0.0145	13.3	25.4
722.5	0.0086	9.05	30.0
708.1	0.0048	6.09	25.2
688.1	0.0035	3.43	36.5
670.2	0.0013	1.73	41.4
<u>47.5 Mole Per Cent ZrF₄</u>			
939	0.496	119	4.5
917.3	0.352	86.4	6.9

TABLE 5. (Continued)

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pLiF	pZrF ₄	
<u>47.5 Mole Per Cent ZrF₄</u>			
(Continued)			
910.2	0.258	74.6	6.0
886.5	0.109	54.1	9.5
876.2	0.158	44.5	15.3
863.1	0.122	38.5	15.3
852.3	0.126	30.3	20.2
839.4	0.0801	23.8	15.8
825.7	0.0278	19.7	15.2
825.6	0.0498	20.9	15.9
813.8	0.0343	16.0	14.3
789.4	0.0251	10.5	21.2
785.3	0.0102	8.55	20.3
779.4	0.0229	9.89	20.2
768.5	0.0131	4.99	21.0
747.2	0.0045	4.44	24.0
746.4	0.0085	4.06	24.9
726.8	0.0066	3.13	28.7
717.2	0.0022	2.15	37.1
704.3	0.0020	1.89	39.8
697.7	0.0023	1.40	49.2
688.2	0.0014	1.30	49.2
675.4	0.0010	0.932	52.5
<u>42.1 Mole Per Cent ZrF₄</u>			
977.0	1.07	101	4.7
961.2	0.727	81.1	5.7
940.1	0.525	56.2	9.4
920.8	0.395	43.9	9.1
903.4	0.286	32.5	13.2
885.6	0.128	24.9	15.2
876.2	0.119	21.6	15.7
874.8	0.111	22.0	15.1
850.8	0.0739	14.3	19.2
823.2	0.0330	8.52	17.4
813.7	0.0406	8.25	18.9
791.1	0.0219	5.02	20.9
778.3	0.0204	4.26	25.6
771.7	0.0144	3.92	28.7
762.9	0.0146	3.02	29.3
752.3	0.0048	2.37	30.3

TABLE 5. (Continued)

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pLiF	pZrF ₄	
<u>42.1 Mole Per Cent ZrF₄</u>			
(Continued)			
742.0	0.0073	1.88	33.1
726.9	0.0033	1.29	41.9
<u>38.8 Mole Per Cent ZrF₄</u>			
1002	1.40	75.1	4.3
977.0	1.04	59.5	6.9
954.7	0.579	40.6	9.4
931.6	0.335	28.6	14.7
910.3	0.245	21.6	14.8
889.6	0.158	16.8	21.7
870.2	0.0948	11.1	20.1
842.4	0.0654	7.79	21.9
831.6	0.0409	5.84	24.4
813.8	0.0358	4.34	23.8
796.4	0.0204	2.91	26.1
779.3	0.0119	2.11	29.6
763.1	0.0124	1.26	48.2
749.0	0.0080	1.00	53.6
731.6	0.0054	0.765	50.1
<u>35.2 Mole Per Cent ZrF₄</u>			
1043	2.89	74.8	4.4
1009	1.36	51.8	7.6
982.0	0.781	32.7	8.6
960.6	0.524	21.1	7.5
938.4	0.417	17.9	8.7
917.1	0.244	15.0	9.7
903.3	--	12.2	10.6
889.7	0.165	7.59	10.4
876.1	0.138	5.70	10.8
856.0	0.0963	4.88	9.4
837.9	0.0645	2.91	10.6
819.5	0.0359	2.64	9.4
802.0	0.0238	1.21	10.1
779.4	0.0088	1.23	51.5
759.5	0.0085	0.661	48.2
736.9	0.0031	0.406	49.3

TABLE 5. (Continued)

Temperature, C	Partial Pressure, mm of mercury		Flow Rate of Carrier Gas, cm ³ per min
	pLiF	pZrF ₄	
<u>27.3 Mole Per Cent ZrF₄</u>			
1058	1.82	21.7	6.3
1044	1.13	18.1	6.2
1009	0.582	10.5	7.9
979.8	0.404	7.11	8.4
963.4	0.268	5.19	9.6
946.2	0.203	3.64	11.0
931.6	0.180	3.14	9.4
916.5	0.111	2.64	9.6
903.3	0.0909	2.23	9.4
887.9	0.0645	1.25	9.7
877.5	0.0837	--	10.4
876.2	0.0546	1.39	16.0
864.1	0.0388	0.885	9.6
851.7	0.0381	0.657	10.3
838.0	0.0208	0.501	49.7
814.6	0.0113	0.474	50.7
<u>16.3 Mole Per Cent ZrF₄</u>			
1060	1.32	2.00	15.0
1033	0.817	1.26	15.0
1026	0.621	1.13	10.9
1017	--	1.05	15.0
1010	0.592	0.833	8.2
1009	0.440	0.815	16.7
1002	0.501	0.750	17.7
984.7	0.375	0.611	21.6
976.0	0.357	--	8.5
974.8	0.259	0.436	16.7
962.1	0.228	0.388	26.3
946.7	0.133	0.290	16.7
940.1	--	0.307	30.2
917.3	0.109	0.185	41.6
916.6	0.0877	0.108	16.4
903.6	0.0644	0.109	20.3
897.3	0.0594	0.100	50.6
888.6	0.0472	0.0729	51.6
876.2	0.0445	0.0713	48.9
862.1	0.0260	0.0616	49.8
851.0	0.0224	0.0395	29.6
838.1	0.0183	0.0244	50.6
827.2	0.0143	0.0182	51.3

FIGURE 8. PARTIAL PRESSURES OF ZrF_4 FOR THE LiF-ZrF_4 SYSTEM ON THE BASIS THAT ONLY LiF AND ZrF_4 EXIST IN THE VAPOR PHASE

Figures on plot denote mole per cent ZrF_4 .

FIGURE 9. VAPOR PRESSURE OF LiF AND PARTIAL PRESSURE OF LiF FOR 16.3 MOLE PER CENT ZrF_4 COMPOSITION OF THE $LiF-ZrF_4$ SYSTEM ON THE BASIS THAT ONLY LiF AND ZrF_4 EXIST IN THE VAPOR PHASE

FIGURE 10. PARTIAL PRESSURES OF LiF FOR 27.3 AND 35.2 MOLE PER CENT ZrF₄ COMPOSITIONS OF THE LiF-ZrF₄ SYSTEM ON THE BASIS THAT ONLY LiF AND ZrF₄ EXIST IN THE VAPOR PHASE

FIGURE 11. PARTIAL PRESSURES OF LiF FOR 38.8 AND 42.1 MOLE PER CENT ZrF_4 COMPOSITIONS OF THE $LiF-ZrF_4$ SYSTEM ON THE BASIS THAT ONLY LiF AND ZrF_4 EXIST IN VAPOR PHASE

FIGURE 12. PARTIAL PRESSURES OF LiF FOR 47.5 MOLE PER CENT ZrF_4 COMPOSITION OF THE $LiF-ZrF_4$ SYSTEM ON THE BASIS THAT ONLY LiF AND ZrF_4 EXIST IN THE VAPOR PHASE

FIGURE 13. PARTIAL PRESSURES OF LiF FOR 61.8 AND 82 MOLE PER CENT ZrF_4 COMPOSITIONS OF THE LiF- ZrF_4 SYSTEM ON THE BASIS THAT ONLY LiF AND ZrF_4 EXIST IN THE VAPOR PHASE

FIGURE 14. PARTIAL PRESSURES OF LiF-ZrF₄ SYSTEM AT 890 C ON THE BASIS THAT ONLY LiF AND ZrF₄ EXIST IN THE VAPOR PHASE

FIGURE 15. PARTIAL PRESSURES OF LiF-ZrF_4 SYSTEM AT 890 C

FIGURE 16. LIQUIDUS CURVES IN THE ZrF_4 -RICH REGION FOR THE NaF -, LiF -, AND RbF-ZrF_4 SYSTEMS

TABLE 6. DERIVED VAPOR-PRESSURE CONSTANTS FOR THE LiF-ZrF_4 SYSTEM ON THE BASIS THAT THE VAPOR PHASE IS COMPOSED OF LiF , ZrF_4 AND LiZr_2F_9

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

Composition, mole per cent ZrF_4	$p\text{LiZr}_2\text{F}_9$		$p\text{ZrF}_4$		$p\text{LiF}$	
	A	B	A	B	A	B
82	--(a)	--(a)	10.478	9.053	--	--
61.8	9.643	11.858	10.095	9.079	--	--
47.5	9.541	11.844	9.612	9.147	--	--
42.1	9.514	11.899	9.332	9.193	--	--
38.8	9.517	11.976	9.313	9.471	--	--
35.2	9.435	11.995	9.318	9.822	--	--
27.3	9.534	12.532	9.412	10.814	--	--
16.3	--	--	8.833	11.585	9.081	12.121

(a) See Figure 13.

Additional Information on the NaF-ZrF₄ System

Gaseous Molecular Complexes

The work on both the RbF-ZrF₄ and LiF-ZrF₄ systems has shown that the complex molecule in the vapor phase consists of two molecules of ZrF₄ and one molecule of the other component. In conducting the work on the NaF-ZrF₄ system, the peak of the p'NaF curve as a function of composition had not been attained.⁽¹⁾ The assumption was made at that time that the simple NaZrF₅ complex exists in the vapor phase. In view of the results obtained from the recent work on the LiF-ZrF₄ and RbF-ZrF₄ systems, it was thought advisable to again attempt to obtain NaF data for the 50 and 74 mpc's. The results are given in Table 7 and Figure 17. From the pressure-composition plot (Figure 18) it is obvious that the peak of the p'NaF curve is not at 50 mpc as previously supposed. Of course, more data would have to be obtained to determine whether the peak occurs at 66.7 or 75 mpc. However, it seems reasonable to assume that for the NaF-ZrF₄ system, the same type of molecular complex exists as is evident for the LiF-ZrF₄ and RbF-ZrF₄ systems. This means that the peak of the p'NaF curve is at 66.7 mpc and that the vapor-phase complex is NaZr₂F₉.

TABLE 7. ADDITIONAL VAPOR-PRESSURE DATA IN THE NaF-ZrF₄ SYSTEM

Temperature, C	Partial Pressure, mm of mercury pNaF	Flow Rate of Carrier Gas, cm ³ per mm
<u>74 Mole Per Cent ZrF₄</u>		
870.4	1.94	6.1
854.3	4.28	5.8
824.4	2.06	10.4
780.6	0.402	18.7
757.3	0.233	19.5
<u>50 Mole Per Cent ZrF₄</u>		
961.7	4.37	5.1
896.0	1.95	14.7
850.6	0.481	14.6
800.4	0.144	24.7
759.2	0.106	26.4
701.3	0.0439	50.6

FIGURE 17. PARTIAL PRESSURES OF NaF FOR THE NaF-ZrF₄ SYSTEM ON THE BASIS THAT ONLY NaF AND ZrF₄ EXIST IN THE VAPOR PHASE

Curves for 38.0 and 41.9 mole per cent ZrF₄ were obtained from BMI-1064.

FIGURE 18. PARTIAL PRESSURE OF NaF FOR NaF-ZrF₄ SYSTEM AT 890 C ON THE BASIS THAT ONLY NaF AND ZrF₄ EXIST IN THE VAPOR PHASE

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