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Thermodynamic Functions from Spectroscopic Data for Some Alkali Fluorides

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Thermodynamic functions were calculated from spectroscopic data for $^7Li_2F_2$, Na_2F_2, and $LiNaF_2$. The results for $^7Li_2F_2$ and Na_2F_2 are comparable with the data of JANAF tables. For the last molecule ($LiNaF_2$) the thermodynamic functions have not been given before.

Harmonic force field analyses have recently been performed [1] for Li_2F_2, Na_2F_2, and $LiNaF_2$ on the basis of observed infrared spectra [2] by the matrix isolation technique. Isotopic molecules with ^6Li and ^7Li were considered in these investigations. In the present work, the adopted structure parameters [1] along with the assigned vibrational frequencies [1,2] are used to calculate thermodynamic functions for $^7Li_2F_2$, Na_2F_2 and $^7LiNaF_2$. Standard methods of calculation are employed.

For $^7Li_2F_2$, the following frequencies [1,2] (in cm^{-1}) were used in the calculations: 641, 553, (551), (524), (342), 287. Parenthesized values are calculated frequencies. The calculated thermodynamic functions at temperatures up to 2000°K are shown in Table 1. The results are comparable with those of the JANAF tables,[3] and are believed to represent slight improvements. Our value of $S°$ (1000°K) = 84.44 e.u. agrees perfectly with 84.4 ± 2 e.u. from Sidorov and Kolosov,[4] although they had applied vibrational frequencies from Berkowitz,[5] which have been disproved by later experiments.

For Na_2F_2, the following frequencies [1,2] (in cm^{-1}) were adopted: 380, 363, (320), (293), (287), < 190. Parenthesized values are calculated frequencies. Successive calculations of thermodynamic functions were performed using 190, 170, and 150 cm^{-1} as the lowest frequency. The results with 170 cm^{-1} are given in Table 2. The influence from ± 20 cm^{-1} in the lowest frequency is about ± 0.1 units on C_p and $(H° - H_0°)/T$, and about ± 0.2 units on $-(F° - H_0°)/T$ and $S°$. Again the present data are believed to give slight im-

Table 1. Thermodynamic functions (cal degree^{-1} mol^{-1}) for $^7Li_2F_2$.

T (°K)	$C_p°$	$(H°-H_0°)/T$	$-(F°-H_0°)/T$	$S°$
100	9.03	8.18	41.26	49.43
200	12.93	9.57	47.31	56.88
300	15.69	11.20	51.50	62.69
400	17.20	12.53	54.91	67.44
500	18.05	13.56	57.82	71.38
600	18.56	14.35	60.37	74.72
700	18.89	14.98	62.63	77.60
800	19.11	15.48	64.66	80.14
900	19.26	15.89	66.51	82.40
1000	19.38	16.24	68.20	84.44
1100	19.46	16.53	69.76	86.29
1200	19.52	16.77	71.21	87.98
1300	19.57	16.99	72.56	89.55
1400	19.62	17.17	73.83	91.00
1500	19.65	17.34	75.02	92.36
1600	19.67	17.48	76.14	93.63
1700	19.70	17.61	77.21	94.82
1800	19.72	17.73	78.22	95.94
1900	19.73	17.83	79.18	97.01
2000	19.75	17.93	80.10	98.02

Table 2. Thermodynamic functions (cal degree^{-1} mol^{-1}) for Na_2F_2.

T (°K)	$C_p°$	$(H°-H_0°)/T$	$-(F°-H_0°)/T$	$S°$
100	11.3	8.9	45.3	54.5
200	16.1	11.4	50.8	64.0
300	17.9	13.3	54.1	70.9
400	18.7	14.6	56.4	76.2
500	19.1	15.5	58.1	80.4
600	19.3	16.1	59.6	83.9
700	19.5	16.6	60.8	86.9
800	19.6	16.9	61.9	89.5
900	19.6	17.2	62.8	91.8
1000	19.7	17.5	63.6	93.9
1100	19.7	17.7	64.4	95.8
1200	19.7	17.8	65.1	97.5
1300	19.8	18.0	65.7	99.1
1400	19.8	18.1	66.3	100.5
1500	19.8	18.2	66.9	101.9
1600	19.8	18.3	67.4	103.2
1700	19.8	18.4	67.9	104.4
1800	19.8	18.5	68.3	105.5
1900	19.8	18.6	68.7	106.6
2000	19.8	18.6	69.1	107.6

provements of the JANAF tables.[3] Our value of $S°$ (1000°K) = 93.9 ± 0.2 e.u. agrees with 94 e.u. from Sidorov and Kolosov,[4] who again had applied frequencies from Berkowitz.[5]

For $^7LiNaF_2$, the following frequencies [1,2] (in cm^{-1}) were used in the calculations: 660, 589, 376, 326, (321), 238. Thermodynamic functions for this molecule have not been given before. The results of our calculations are shown in Table 3.

Table 3. Thermodynamic functions (cal $degree^{-1}$ mol^{-1}) for $^7LiNaF_2$.

T (°K)	$C_p°$	$(H°-H_0°)/T$	$-(F°-H_0°)/T$	$S°$
100	9.90	8.41	45.00	53.41
200	14.14	10.29	51.39	61.68
300	16.50	12.01	55.90	67.91
400	17.74	13.30	59.54	72.84
500	18.42	14.26	62.62	76.88
600	18.83	14.99	65.29	80.28
700	19.09	15.56	67.64	83.20
800	19.26	16.01	69.75	85.76
900	19.39	16.38	71.66	88.04
1000	19.48	16.69	73.40	90.09
1100	19.54	16.94	75.00	91.95
1200	19.60	17.16	76.49	93.65
1300	19.64	17.35	77.87	95.22
1400	19.67	17.52	79.16	96.68
1500	19.69	17.66	80.37	98.03
1600	19.71	17.79	81.52	99.31
1700	19.73	17.90	82.60	100.50
1800	19.75	18.00	83.63	101.63
1900	19.76	18.10	84.60	102.70
2000	19.77	18.18	85.53	103.71

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