# Heat capacities and thermodynamic properties of Li$_{0.5}$Fe$_{2.5}$O$_4$ and Li$_{0.5}$Al$_{2.5}$O$_4$ from 5 to 545 K

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The heat capacities of Li$_{0.5}$Fe$_{2.5}$O$_4$ and Li$_{0.5}$Al$_{2.5}$O$_4$ were measured by adiabatic calorimetry from 5 to 545 K and no transitions or thermal anomalies were found. The low-temperature heat capacity of Li$_{0.5}$Fe$_{2.5}$O$_4$ shows the $T^{3/2}$ dependence expected for a ferrimagnetic substance. Lattice and spin-wave contributions to the heat capacity were calculated and compared with Pollack's values. The heat capacities of both compounds above 300 K are in good agreement with values obtained by Kopp's rule based on the component oxides. At 298.15 K, the heat capacity at constant pressure $C_p$, the entropy $S°$, and the function $[\{G°(T) - H°(0)\}/T]$ are 34.43, 29.20, and $-11.811$ cal$_{th}$ K$^{-1}$ mol$^{-1}$ for Li$_{0.5}$Fe$_{2.5}$O$_4$; 26.79, 17.899, and $-6.246$ cal$_{th}$ K$^{-1}$ mol$^{-1}$ for Li$_{0.5}$Al$_{2.5}$O$_4$. For the latter compound at 298.15 K $\Delta H_f° = -(541 \pm 2)$ kcal$_{th}$ mol$^{-1}$ and $\Delta G_f° = -(535 \pm 2)$ kcal$_{th}$ mol$^{-1}$.

## 1. Introduction

The refractory compounds Li$_{0.5}$Fe$_{2.5}$O$_4$ and Li$_{0.5}$Al$_{2.5}$O$_4$ with their inverse-spinel structure are of considerable interest both scientifically and technologically. Lithium ferrite (Li$_{0.5}$Fe$_{2.5}$O$_4$) has been studied extensively[1] not only because of the interesting ordering of the lithium ions below 1040 K, but also because of its excellent square magnetic hysteresis and its consequent application in computer memory cores. Lithium aluminate spinel (Li$_{0.5}$Al$_{2.5}$O$_4$) has been used widely[2–5] as a host lattice for the study of the effects of dopants in octahedral and tetrahedral environments. Disks of the aluminate have been recently hot pressed into a transparent ceramic for possible application as a high-temperature optical material. The heat capacities and thermodynamic functions obtained in this study together with thermochemical data—as they become available—will give a complete thermodynamic picture of these important substances.

## 2. Experimental

### PREPARATION AND CHARACTERIZATION OF SAMPLES

Lithium ferrite and aluminate were prepared by solid-state reactions between lithium carbonate and aluminum and iron sesquioxides. The lithium carbonate was Baker's Analytical Reagent Grade, the iron(III) oxide was Baker's Reagent Grade, and the

aluminum oxide was Semiconductor Grade from the Linde Division of the Carborundum Corporation. The reactants were well mixed mechanically and then pressed into pellets in a steel die using pressures up to $10^5$ kPa. The ferrite powder was reacted in air at 1050 to 1150 K, ground in a steel mortar, sieved, repelleted, and refired at 1350 K. The aluminate was similarly treated but the corresponding temperatures were 1350 to 1500 K and 1550 K. After the final firing the products were annealed for 10 days and slowly cooled to room temperature. The annealing temperatures were 900 K for lithium ferrite and 1300 K for the aluminate sample. The annealed products were characterized by X-ray diffraction using a Guinier-Häag camera with Cu-K$\alpha_1$ radiation and by chemical analysis. The diffraction patterns of both compounds revealed no second phases, and the refined lattice parameters (based on 13 lines for the ferrite, and 17 for the aluminate[6]) agreed well with the accepted values. The lattice parameters for lithium ferrite and lithium aluminate obtained in this work were $(0.8330 \pm 0.0001)$ nm and $(0.7906 \pm 0.0002)$ nm, respectively; these accord well with the accepted values $(0.8331 \pm 0.0002)$ nm,[7] and $(0.7907 \pm 0.0001)$ nm.[8] Chemical analyses for lithium and iron made on the lithium ferrite sample indicated: Fe, $(67.16 \pm 0.24)$ mass per cent (theoretical, 67.42 mass per cent); and Li, $(1.70 \pm 0.03)$ mass per cent (theoretical, 1.68 mass per cent). The lithium analysis for the aluminate sample was $(5.63 \pm 0.05)$ mass per cent of $Li_2O$ (theoretical, 5.54 mass per cent).

## CRYOSTAT AND CALORIMETERS

The low-temperature heat capacities of $Li_{0.5}Fe_{2.5}O_4$ and $Li_{0.5}Al_{2.5}O_4$ were determined in the Mark II adiabatic cryostat described in detail elsewhere.[9] Temperatures are based on a thermometer calibration by the National Bureau of Standards and are believed to agree with the International Practical Temperature Scale (1948, revised 1960) within 0.04 K from 90 to 350 K, 0.03 K from 10 to 90 K, and within 0.1 K from 4 to 10 K.

Information on the loading of both compounds in the cryostat and thermostat used is summarized in table 1. The top of calorimeter W-16 was sealed in place with

TABLE 1. Calorimeter loading information: volume $V$ of calorimeter,
sample mass $m$, density $\rho$, and He pressure $p$
{Torr = (101.325/760) kPa}

| Compound | Calorimeter designation | $\dfrac{V}{cm^3}$ | $\dfrac{m}{g}$ | $\dfrac{\rho}{g\,cm^{-3}}$ | $\dfrac{p}{Torr}$ |
|---|---|---|---|---|---|
| | | Low-temperature determinations Mark-II cryostat (A-5 thermometer) | | | |
| $Li_{0.5}Fe_{2.5}O_4$ | W-16 | 73 | 124.905 | 4.75 | 51 |
| $Li_{0.5}Al_{2.5}O_4$ | W-48 | 44 | 50.652 | 3.28 | 66 |
| | | Higher-temperature determinations Mark IV thermostat (A-8 thermometer) | | | |
| $Li_{0.5}Fe_{2.5}O_4$ | W-22-P | 84 | 124.447 | | 114 |
| $Li_{0.5}Al_{2.5}O_4$ | W-22-P | 84 | 52.857 | | 110.5 |

Cerroseal-35 (indium + tin solder). The loaded calorimeter was then evacuated at room temperature for about an hour through a small hole in the helium seal-off tube and 51 Torr of pure helium was admitted to the calorimeter to assure thermal contact between calorimeter and sample.† The calorimeter was then sealed with Cerroseal-35 with a soldering iron operating within the vacuum chamber. The amounts of solder and Apiezon-T grease (used to assist in establishing equilibration between the thermometer-heater assembly and the calorimeter) were adjusted carefully to the amounts present during the determination of the heat capacity of the empty calorimeter. The procedure used to determine the heat capacity of lithium aluminate was the same as described above except that a screw-type closure calorimeter, similar to one described elsewhere,[10] was used.

The heat-capacity determinations in the range 300 to 550 K were made in the previously described Mark IV adiabatic thermostat[11] which has two internal shields that are controlled automatically. A third automatic control operates a guard shield that surrounds the two adiabatic shields and the calorimeter and minimizes the heat leak between the shields and surroundings. The experimental procedure used was very similar to that for the determination of heat capacities in the Mark II cryostat.

## 3. Results

The experimental values of the molar heat capacities of lithium ferrite and aluminate are given in chronological order, in tables 2 and 3, and are depicted in figure 1. These values have been adjusted to the true heat capacities by applying a curvature correction for the finite temperature increments used in the measurements. The ice point is taken to be 273.15 K and the molar masses of $Li_{0.5}Fe_{2.5}O_4$ and $Li_{0.5}Al_{2.5}O_4$ were taken to be 207.085 and 134.921 g mol$^{-1}$ respectively on the 1968 scale of relative atomic masses. The molar heat capacity and thermodynamic functions derived from the heat capacities are listed at selected temperatures in tables 4 and 5. These heat capacities were obtained by a digital computer and are estimated to have a probable error of 0.1 per cent above 25 K, and 1 per cent at 14 K increasing to about 5 per cent at 5 K.

LITHIUM FERRITE

The heat capacity of lithium ferrite was extrapolated below 5 K by using an equation of the form $C_p = aT^3 + bT^{3/2}$ where $a$ and $b$ were obtained from a least-squares treatment of the plot of $C_p/T^{3/2}$ against $T^{3/2}$, shown in figure 2. The values of $a$ and $b$ obtained in this work ($(13 \pm 5)$ $\mu cal_{th}$ K$^{-4}$ mol$^{-1}$ and $(160 \pm 2)$ $\mu cal_{th}$ K$^{-5/2}$ mol$^{-1}$) may be compared with those of Pollack and Atkins[12] ($(24 \pm 1)$ $\mu cal_{th}$ K$^{-4}$ mol$^{-1}$ and $(162 \pm 4)$ $\mu cal_{th}$ K$^{-5/2}$ mol$^{-1}$, respectively). Although the values of $b$ obtained from both studies are well within the calculated standard deviations, there is no apparent explanation for the discrepancy in the values for $a$.

Above 298 K the heat capacity of lithium ferrite has been measured by Reznitzkii et al. by the continuous heating method[13] under adiabatic conditions. Using this

† Throughout this paper Torr = (101.325/760) kPa, $cal_{th}$ = 4.184 J.

47

TABLE 2. Heat capacity of $Li_{0.5}Fe_{2.5}O_4$

($cal_{th}$ = 4.184 J)

| $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$ |
|---|---|---|---|---|---|---|---|
| | | | Mark II | Cryostat | | | |
| | Series I | 266.33 | 32.040 | 81.07 | 7.289 | 10.62 | 0.019 |
| 147.55 | 18.431 | 273.43 | 32.571 | 87.92 | 8.480 | 10.81 | 0.021 |
| 155.93 | 19.693 | | | 99.28 | 10.415 | 11.21 | 0.024 |
| 163.91 | 20.855 | | | 113.01 | 12.757 | 11.39 | 0.026 |
| 171.56 | 21.919 | | Series IV | 116.08 | 13.282 | 11.50 | 0.028 |
| 179.10 | 22.932 | 269.69 | 32.308 | 126.14 | 14.977 | 11.98 | 0.027 |
| 186.90 | 23.921 | 276.74 | 32.865 | 135.30 | 16.475 | 12.29 | 0.030 |
| | | 283.69 | 33.361 | 143.84 | 17.837 | 13.14 | 0.037 |
| | | 290.57 | 33.850 | 151.90 | 19.084 | 13.56 | 0.042 |
| | Series II | 297.36 | 34.384 | 159.56 | 20.217 | 15.28 | 0.057 |
| 186.36 | 23.839 | 304.56 | 34.869 | 166.91 | 21.268 | 16.31 | 0.073 |
| 194.25 | 24.822 | 312.16 | 35.404 | 173.98 | 22.244 | 17.31 | 0.088 |
| 201.91 | 25.749 | 319.69 | 35.817 | | | 18.51 | 0.111 |
| | | 327.49 | 36.380 | | | 20.29 | 0.149 |
| | | 335.59 | 36.803 | | Series VI | 22.66 | 0.220 |
| | Series III | 343.61 | 37.197 | 7.37 | 0.0081 | 24.93 | 0.305 |
| 197.78 | 25.243 | | | 8.18 | 0.011 | 27.25 | 0.414 |
| 205.30 | 26.115 | | | 8.53 | 0.012 | 29.88 | 0.562 |
| 213.10 | 26.998 | | Series V | 8.95 | 0.018 | 30.20 | 0.581 |
| 221.19 | 27.845 | 49.93 | 2.523 | 9.33 | 0.016 | 33.02 | 0.778 |
| 229.09 | 28.656 | 53.68 | 3.013 | 9.35 | 0.016 | 35.74 | 0.995 |
| 236.81 | 29.411 | 57.92 | 3.601 | 9.67 | 0.017 | 39.23 | 1.313 |
| 244.38 | 30.144 | 63.64 | 4.459 | 10.03 | 0.019 | 43.57 | 1.767 |
| 251.82 | 30.811 | 69.99 | 5.447 | 10.15 | 0.020 | 47.76 | 2.253 |
| 259.13 | 31.436 | 75.87 | 6.399 | 10.53 | 0.022 | 51.23 | 2.694 |
| | | | Mark IV | Thermostat | | | |
| | Series I | | Series II | 423.89 | 40.82 | | Series IV |
| 300.28 | 34.56 | 332.62 | 36.56 | 434.77 | 41.24 | 481.95 | 42.81 |
| 309.31 | 35.13 | 344.55 | 37.23 | | | 492.48 | 43.16 |
| 318.10 | 35.75 | 356.30 | 37.89 | | Series III | 502.92 | 43.46 |
| 326.79 | 36.25 | 367.90 | 38.48 | 428.62 | 41.00 | 513.28 | 43.76 |
| 335.28 | 36.74 | 379.33 | 38.99 | 439.47 | 41.38 | 523.58 | 43.99 |
| | | 390.64 | 39.50 | 460.88 | 42.14 | 531.03 | 44.25 |
| | | 401.83 | 39.95 | 471.47 | 42.47 | 541.13 | 44.62 |
| | | 412.92 | 40.38 | 481.98 | 42.82 | | |

TABLE 3. Heat capacity of $Li_{0.5}Al_{2.5}O_4$
($cal_{th} = 4.184$ J)

| $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}mol^{-1}}$ | $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\,K^{-1}mol^{-1}}$ |
|---|---|---|---|---|---|---|---|
| | | | | Mark II Cryostat | | | |
| | Series I | 31.44 | 0.136 | | Series III | 196.58 | 17.245 |
| 7.84 | 0.0016 | 34.88 | 0.196 | 94.57 | 4.195 | 207.53 | 18.506 |
| 9.03 | 0.0034 | 38.64 | 0.269 | 105.40 | 5.446 | 218.51 | 19.732 |
| 9.85 | 0.0067 | 43.08 | 0.379 | 115.66 | 6.751 | 229.54 | 20.893 |
| 10.62 | 0.0095 | 48.81 | 0.580 | 125.81 | 8.085 | 240.51 | 21.979 |
| 11.45 | 0.0125 | | | 136.22 | 9.495 | 251.06 | 22.968 |
| 12.45 | 0.0146 | | | 146.93 | 10.960 | 261.40 | 23.895 |
| 13.62 | 0.0205 | | Series II | 157.92 | 12.424 | 271.95 | 24.774 |
| 14.96 | 0.0235 | 47.70 | 0.539 | 168.65 | 13.818 | 282.71 | 25.622 |
| 16.55 | 0.0285 | 52.40 | 0.737 | 179.22 | 15.159 | 293.70 | 26.419 |
| 18.23 | 0.0313 | 58.25 | 1.037 | | | 304.95 | 27.219 |
| 20.00 | 0.0385 | 64.56 | 1.438 | | | 316.62 | 28.038 |
| 21.90 | 0.0431 | 70.72 | 1.879 | | | 328.49 | 28.816 |
| 23.93 | 0.0557 | 77.30 | 2.430 | | Series IV | 340.36 | 29.494 |
| 26.20 | 0.0754 | 85.22 | 3.203 | 175.89 | 14.746 | | |
| 28.68 | 0.102 | 95.13 | 4.252 | 185.94 | 15.991 | | |
| | | | | Mark IV Thermostat | | | |
| | Series I | | Series II | 409.75 | 32.95 | | Series III |
| 313.64 | 27.88 | 330.67 | 28.95 | 419.51 | 33.32 | 462.74 | 34.64 |
| 322.60 | 28.48 | 340.10 | 29.53 | 429.49 | 33.63 | 473.75 | 34.98 |
| 332.03 | 29.08 | 349.39 | 30.10 | 439.71 | 33.91 | 484.68 | 35.24 |
| 341.32 | 29.66 | 358.99 | 30.63 | 449.84 | 34.30 | 495.80 | 35.56 |
| 350.49 | 40.18 | 368.92 | 31.18 | 451.64 | 34.29 | 507.11 | 35.91 |
| | | 378.71 | 31.66 | 460.33 | 34.61 | 518.32 | 36.03 |
| | | 388.40 | 32.10 | | | 529.50 | 36.28 |
| | | 398.00 | 32.49 | | | 540.61 | 36.51 |
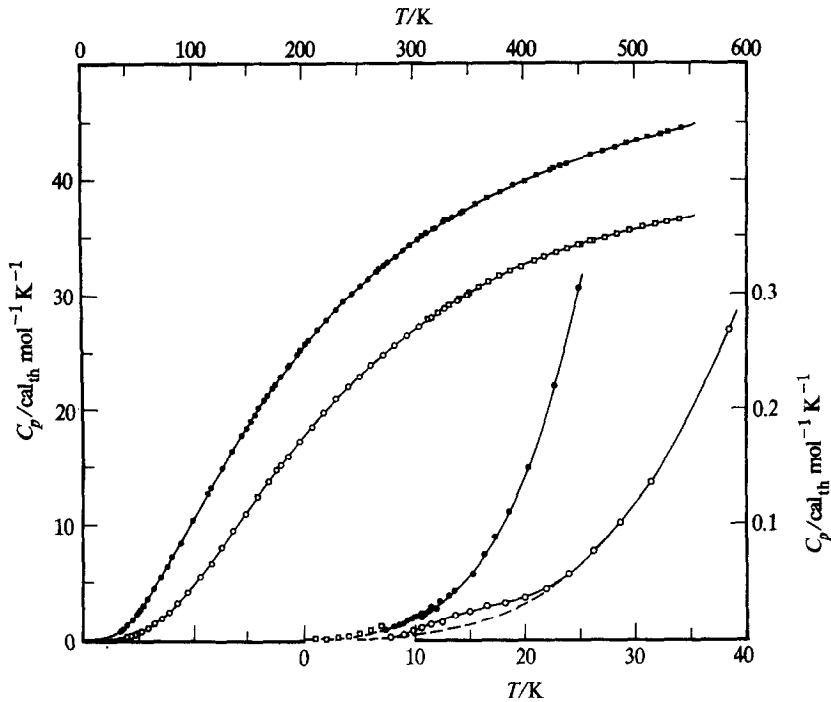
FIGURE 1. Heat capacities of $Li_{0.5}Fe_{2.5}O_4$ and $Li_{0.5}Al_{2.5}O_4$. The experimental heat capacities for the ferrite (upper curves) are represented by ●; those for the aluminate are given by ○ (lower curves).
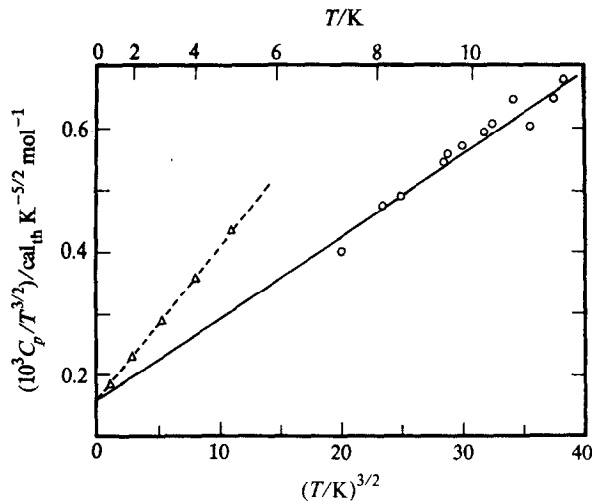


FIGURE 2. Plot for evaluation of the parameters of $C_p = aT^3 + bT^{3/2}$. The results of this research on lithium ferrite are given by ——○——, those of Pollack and Atkins by – – – △ – – –.

TABLE 4. Thermodynamic functions of $Li_{0.5}Fe_{2.5}O_4$

$(cal_{th} = 4.184\ J)$

| $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th}\ K^{-1}\ mol^{-1}}$ | $\dfrac{S^\circ}{cal_{th}\ K^{-1}\ mol^{-1}}$ | $\dfrac{\{H^\circ(T) - H^\circ(0)\}}{cal_{th}\ mol^{-1}}$ | $\dfrac{-\{G^\circ(T)-H^\circ(0)\}/T}{cal_{th}\ K^{-1}\ mol^{-1}}$ |
|---|---|---|---|---|
| 5 | (0.003) | (0.001) | (0.005) | 0.000 |
| 10 | 0.019 | 0.008 | 0.055 | 0.003 |
| 15 | 0.054 | 0.021 | 0.224 | 0.006 |
| 20 | 0.142 | 0.047 | 0.685 | 0.013 |
| 25 | 0.310 | 0.095 | 1.78 | 0.069 |
| 30 | 0.572 | 0.173 | 3.94 | 0.042 |
| 35 | 0.932 | 0.288 | 7.66 | 0.069 |
| 40 | 1.386 | 0.441 | 13.42 | 0.105 |
| 45 | 1.932 | 0.634 | 21.66 | 0.153 |
| 50 | 2.531 | 0.868 | 32.77 | 0.212 |
| 60 | 3.912 | 1.448 | 64.83 | 0.370 |
| 70 | 5.450 | 2.165 | 111.54 | 0.572 |
| 80 | 7.095 | 3.000 | 174.20 | 0.822 |
| 90 | 8.806 | 3.934 | 253.67 | 1.115 |
| 100 | 10.542 | 4.951 | 350.40 | 1.447 |
| 110 | 12.274 | 6.037 | 464.50 | 1.815 |
| 120 | 13.979 | 7.179 | 595.79 | 2.214 |
| 130 | 15.641 | 8.363 | 743.93 | 2.641 |
| 140 | 17.248 | 9.582 | 908.43 | 3.093 |
| 150 | 18.793 | 10.825 | 1088.69 | 3.567 |
| 160 | 20.272 | 12.085 | 1284.07 | 4.060 |
| 170 | 21.628 | 13.357 | 1493.90 | 4.570 |
| 180 | 23.02 | 14.635 | 1717.49 | 5.092 |
| 190 | 24.30 | 15.914 | 1954.15 | 5.629 |
| 200 | 25.51 | 17.191 | 2203.2 | 6.175 |
| 210 | 26.65 | 18.464 | 2464.1 | 6.730 |
| 220 | 27.74 | 19.729 | 2736.0 | 7.292 |
| 230 | 28.76 | 20.98 | 3018.6 | 7.860 |
| 240 | 29.73 | 22.23 | 3311.1 | 8.433 |
| 250 | 30.65 | 23.46 | 3613.0 | 9.009 |
| 260 | 31.52 | 24.68 | 3923.9 | 9.589 |
| 270 | 32.34 | 25.89 | 4243.2 | 10.170 |
| 273.15 | 32.59 | 26.26 | 4345.5 | 10.354 |
| 280 | 33.12 | 27.08 | 4570.6 | 10.753 |
| 290 | 33.86 | 28.25 | 4905.5 | 11.336 |
| 298.15 | 34.43 | 29.20 | 5183.8 | 11.811 |
| 300 | 34.56 | 29.41 | 5247.6 | 11.919 |
| 320 | 35.84 | 31.68 | 5951.8 | 13.084 |
| 340 | 37.00 | 33.89 | 6680.5 | 14.243 |
| 360 | 38.05 | 36.04 | 7431.2 | 15.394 |
| 380 | 39.00 | 38.12 | 8162.9 | 16.479 |
| 400 | 39.88 | 40.14 | 8990.8 | 17.666 |
| 420 | 40.68 | 42.11 | 9796.6 | 18.783 |
| 440 | 41.43 | 44.02 | 10617.8 | 19.887 |
| 460 | 42.11 | 45.88 | 11453.3 | 20.98 |
| 480 | 42.75 | 47.68 | 12302.0 | 22.05 |
| 500 | 43.34 | 49.44 | 13162.9 | 23.11 |
| 520 | 43.93 | 51.15 | 14035.6 | 24.16 |
| 540 | 44.58 | 52.83 | 14920.6 | 25.19 |

TABLE 5. Thermodynamic functions of $Li_{0.5}Al_{2.5}O_4$

$(cal_{th} = 4.184 \text{ J})$

| $\dfrac{T}{K}$ | $\dfrac{C_p}{cal_{th} \, K^{-1} \, mol^{-1}}$ | $\dfrac{S^\circ}{cal_{th} \, K^{-1} \, mol^{-1}}$ | $\dfrac{\{H^\circ(T) - H^\circ(0)\}}{cal_{th} \, mol^{-1}}$ | $\dfrac{-\{G^\circ(T) - H^\circ(0)\}/T}{cal_{th} \, K^{-1} \, mol^{-1}}$ |
|---|---|---|---|---|
| 5 | (0.0005) | (0.0001) | (0.0006) | (0.000) |
| 10 | (0.004) | (0.001) | (0.0097) | (0.000) |
| 15 | (0.013) | (0.004) | (0.0491) | (0.001) |
| 20 | (0.031) | (0.010) | (0.155) | (0.002) |
| 25 | 0.066 | 0.021 | 0.381 | 0.006 |
| 30 | 0.118 | 0.038 | 0.834 | 0.010 |
| 35 | 0.190 | 0.061 | 1.593 | 0.015 |
| 40 | 0.296 | 0.093 | 2.793 | 0.023 |
| 45 | 0.442 | 0.126 | 4.196 | 0.031 |
| 50 | 0.631 | 0.192 | 7.287 | 0.046 |
| 60 | 1.137 | 0.349 | 15.982 | 0.082 |
| 70 | 1.819 | 0.573 | 30.62 | 0.136 |
| 80 | 2.674 | 0.870 | 52.96 | 0.208 |
| 90 | 3.682 | 1.242 | 84.62 | 0.302 |
| 100 | 4.813 | 1.687 | 127.00 | 0.417 |
| 110 | 6.037 | 2.203 | 181.19 | 0.556 |
| 120 | 7.326 | 2.783 | 248.0 | 0.717 |
| 130 | 8.655 | 3.422 | 327.8 | 0.900 |
| 140 | 10.002 | 4.112 | 421.1 | 1.104 |
| 150 | 11.350 | 4.848 | 527.9 | 1.329 |
| 160 | 12.683 | 5.623 | 648.1 | 1.573 |
| 170 | 13.990 | 6.432 | 781.4 | 1.835 |
| 180 | 15.262 | 7.268 | 927.7 | 2.113 |
| 190 | 16.491 | 8.126 | 1086.5 | 2.407 |
| 200 | 17.674 | 9.002 | 1257.4 | 2.715 |
| 210 | 18.809 | 9.892 | 1439.9 | 3.036 |
| 220 | 19.893 | 10.792 | 1633.4 | 3.368 |
| 230 | 20.93 | 11.699 | 1837.5 | 3.710 |
| 240 | 21.91 | 12.611 | 2051.8 | 4.062 |
| 250 | 22.85 | 13.525 | 2275.6 | 4.422 |
| 260 | 23.75 | 14.439 | 2508.7 | 4.790 |
| 270 | 24.60 | 15.351 | 2750.4 | 5.164 |
| 273.15 | 24.86 | 15.638 | 2828.3 | 5.283 |
| 280 | 25.41 | 16.260 | 3000.4 | 5.544 |
| 290 | 26.18 | 17.165 | 3258.4 | 5.929 |
| 298.15 | 26.79 | 17.899 | 3474.3 | 6.246 |
| 300 | 26.92 | 18.065 | 3523.9 | 6.319 |
| 320 | 28.30 | 19.847 | 4076.3 | 7.109 |
| 340 | 29.54 | 21.60 | 4654.9 | 7.910 |
| 360 | 30.67 | 23.32 | 5257.2 | 8.718 |
| 380 | 31.67 | 25.01 | 5880.9 | 9.532 |
| 400 | 32.56 | 26.66 | 6523.4 | 10.347 |
| 420 | 33.33 | 28.26 | 7182.4 | 11.162 |
| 440 | 34.00 | 29.83 | 7855.8 | 11.975 |
| 460 | 34.59 | 31.35 | 8541.7 | 12.784 |
| 480 | 35.13 | 32.84 | 9239.0 | 13.589 |
| 500 | 35.64 | 34.28 | 9946.7 | 14.388 |
| 520 | 36.11 | 35.69 | 10664.2 | 15.180 |
| 540 | 36.50 | 37.06 | 11390.6 | 15.965 |

method, more than 400 determinations were made by Reznitzkii $et$ $al.$[14] at 5 to 6 K intervals with a reproducibility of under 1 per cent in a non-magnetic stainless-steel calorimeter with a Pt-to-(Pt+13 mass per cent Rh) thermocouple for measuring temperature. Although no explanation is available for the fact that their data are 9 per cent higher than ours at 300 K, 2 per cent lower at 400 K, and 7 per cent lower at 500 K, it is worth while to note that in determining the heat capacity of their empty calorimeter[14] an anomalous heat capacity against temperature curve was obtained, where the apparent heat capacity of the calorimeter decreased with temperature in the temperature range 298 to 600 K.

## LITHIUM ALUMINATE

Values from 5 K to 0 were extrapolated by the Debye limiting law. A small rounded anomaly with an excess entropy of $6.4 \times 10^{-3}$ $cal_{th}$ $K^{-1}$ $mol^{-1}$ was found between 10 and 22 K and assumed to be due to impurities in the sample. The entropy and enthalpy associated with this anomaly were not included in the tabulated molar thermodynamic functions given in table 5.

TABLE 6. Comparison with Kopp's rule based on component oxides $^a$

($cal_{th}$ = 4.184 J)

| $\dfrac{T}{K}$ | $\dfrac{C_p(\text{expt})}{cal_{th}\ K^{-1}\ mol^{-1}}$ | $\dfrac{C_p(\text{Kopp})}{cal_{th}\ K^{-1}\ mol^{-1}}$ $^b$ | $\dfrac{10^2\{C_p(\text{expt}) - C_p(\text{Kopp})\}}{C_p(\text{expt})}$ |
|---|---|---|---|
| | $Li_{0.5}Fe_{2.5}O_4$ | | |
| 300 | 34.56 | 34.67 | −0.32 |
| 350 | 37.54 | 37.46 | +0.21 |
| 400 | 39.88 | 39.71 | +0.46 |
| 450 | 41.78 | 41.64 | +0.33 |
| 500 | 43.34 | 43.37 | −0.07 |
| | $Li_{0.5}Al_{2.5}O_4$ | | |
| 300 | 26.92 | 27.24 | −1.1 |
| 350 | 30.12 | 30.33 | −0.69 |
| 400 | 32.55 | 32.47 | +0.02 |
| 450 | 34.30 | 34.03 | +0.81 |
| 500 | 35.64 | 35.26 | +1.1 |

$^a$ $C_p(Li_2O)$, reference 17; $C_p(Fe_2O_3)$, reference 19; $C_p(Al_2O_3)$, reference 16.
$^b$ $C_p(Li_{0.5}M_{2.5}O_4) = 0.25C_p(Li_2O) + 1.25C_p(M_2O_3)$.

Kopp's rule has been applied successfully to the calculation of the heat capacities of silicates and titanates[18] in terms of the component oxides and would be expected to give very good results when applied to aluminates and to ferrites below their Curie temperatures. That this is so for lithium aluminate and ferrite from 300 to 500 K is shown in table 6. By employing heat capacities of lithium aluminate from 500 to 968 K obtained from Kopp's rule, the enthalpy of formation of $Li_{0.5}Al_{2.5}O_4$ from the component oxides measured[15] at 968 K has been used in conjunction with the pertinent thermodynamic properties of $Al_2O_3$,[16] and $Li_2O$,[17] from

critical tabulations to obtain the standard enthalpy and Gibbs energy of formation for $Li_{0.5}Al_{2.5}O_4$ at 298.15 K. These values are $-(543\pm2)$ $kcal_{th}\,mol^{-1}$ and $-(535\pm2)\,kcal_{th}\,mol^{-1}$, respectively.

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