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Heat capacity of γ -Fe₂SiO₄ between 5 and 303 K and derived thermodynamic properties

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Abstract A multi-anvil device was used to synthesize 24 mg of pure γ -Fe₂SiO₄ crystals at 8.5 GPa and 1,273 K. The low-temperature heat capacity (C_p) of y-Fe₂SiO₄ was measured between 5 and 303 K using the heat capacity option of a physical properties measurement system. The measured heat capacity data show a broad λ -transition at 11.8 K. The difference in the C_p between fayalite and γ -Fe₂SiO₄ is reduced as the temperature increases in the range of 50-300 K. The gap in C_p data between 300 and 350 K of γ -Fe₂SiO₄ is an impediment to calculation of a precise C_p equation above 298 K that can be used for phase equilibrium calculations at high temperatures and high pressures. The C_p and entropy of γ -Fe₂SiO₄ at standard temperature and pressure (S°_{298}) are 131.1 ± 0.6 and $140.2 \pm 0.4 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The Gibbs free energy at standard pressure and temperature ($\Delta G^{\circ}_{f,298}$) is calculated to be $-1,369.3 \pm 2.7$ J mol⁻¹ based on the new entropy data. The phase boundary for the fayalite-y-Fe₂SiO₄ transition at 298 K based on current thermodynamic data is located at 2.4 \pm 0.6 GPa with a slope of 25.4 bars/K, consistent with extrapolated results of previous experimental studies.

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Introduction

Calorimetric measurements of the heat capacity $(C_{\rm p})$ of many high-pressure phases are incomplete. The entropy value is critical to thermodynamic calculations of the phase equilibrium relations, and the most precise way to obtain the entropy value is by measuring the heat capacity as a function of temperature. However, high-pressure phases must be synthesized experimentally in a multi-anvil device, and the minimum amount of sample needed for low-temperature heat capacity measurement by conventional low-temperature adiabatic calorimetry (low-TAC, e.g., Robie and Hemingway 1972), which is 10-30 g in general, would take hundreds of experimental runs just to make enough sample, hence prohibiting the heat capacity measurement in practice. Recently, the heat capacity option of the Physical Properties Measurement System (PPMS, produced by Quantum Design[®]), based on heat-pulse calorimetry, has been shown to give precise low-temperature heat capacity measurements of milligramsized samples (e.g., Dachs and Bertoldi 2005; Yong et al. 2006).

Fayalite (Fe₂SiO₄) is one end-member of olivine, the most abundant mineral in the earth's upper mantle. Numerous experimental studies on Fe₂SiO₄ have shown that fayalite transforms into a phase with a spinel structure (γ -Fe₂SiO₄) at pressures higher than 4– 5 GPa at 700–1,300 K (e.g., Akimoto et al. 1965, 1967; Inoue 1975; Sung and Burns 1976; Furnish and Bassett

1983; Yagi et al. 1987). The natural occurrence of γ - Fe_2SiO_4 with Fe/(Fe + Mg) ratios ranging from 0.62 to 0.99 has also been reported in a shocked chondrite meteorite (Xie et al. 2002; Xie and Sharp 2004). The transition in (Mg,Fe)₂SiO₄ is regarded to play an important role in the formation of seismic discontinuities. Therefore, direct measurement of the thermodynamic properties of γ -Fe₂SiO₄ and favalite is of great importance in terms of understanding geophysical applications at mantle conditions. Although the thermodynamic properties of fayalite have been well characterized, those of γ -Fe₂SiO₄ are still in need of characterization. The enthalpy and high-temperature heat capacity of γ -Fe₂SiO₄ were measured by Akaogi et al. (1989) and Watanabe (1982), respectively. However, for the aforementioned reason, the lowtemperature heat capacity and thus entropy value of γ -Fe₂SiO₄ was not determined calorimetrically. In this study, the heat capacity data of γ -Fe₂SiO₄ were measured between 5 and 303 K using the PPMS machine at Salzburg, and the entropy and Gibbs free energy at standard temperature and pressure (STP) were calculated from the measured heat capacity data.

Experimental procedures

Sample synthesis and characterization

Fayalite was synthesized from a stoichiometric mixture of Fe₃O₄ and SiO₂. After mixing in an agate pestle and mortar, the starting material was reacted at 1,200°C for 48 h in a CO-CO₂ gas stream, adjusted to buffer oxygen fugacity at a value of two log units below fayalitemagnetite-quartz equilibrium. A 3-mm diameter Au capsule was loaded with more than 30 mg of fayalite powder and sealed by welding. The γ -Fe₂SiO₄ used in this study was synthesized from pure fayalite starting material in a 1,000-ton Walker-type multi-anvil device at the University of Minnesota. The experimental assemblage consisted of tungsten carbide anvils with 12 mm truncations, a cast MgO-Al₂O₃-SiO₂-Cr₂O₃ octahedron, straight-walled graphite heater and internal MgO spacers. The temperature was controlled using a W₃Re₉₇/W₂₅Re₇₅ thermocouple, which was located on top of the Au capsule with a 0.35-mm disk of MgO extrusion for electrical isolation. The sample was pressurized to 8.5 GPa before heating at 1,273 K for 12 h. The experiment was quenched by turning off the power to the heater and then slowly depressurized to ambient pressure. The run product was examined by powder X-ray diffraction and electron microprobe (EMP) analysis, and single phase γ -Fe₂SiO₄ was confirmed.

Heat capacity measurement

The molar heat capacity at constant pressure (C_p) of γ -Fe₂SiO₄ in the temperature range of 5–303 K was measured at 1 atm using the heat capacity option of the PPMS at Salzburg University in Austria. A powdered sample of γ -Fe₂SiO₄ (24.0 mg) was sealed into a small Al pan with a lid and placed on a 4 mm \times 4 mm wide sapphire platform that has a thermometer and a heater attached to the lower side. The C_p data were first collected at 60 different temperatures from 5 to 303 K with a logarithmic spacing, and three measurements were performed at each temperature. More $C_{\rm p}$ data were collected around 12 K and from 50 to 303 K with a linear spacing in a second run. A brief summary of this technique is given by Yong et al. (2006), and a more detailed description including discussions of the precision and accuracy of the C_p measurement by PPMS is in Lashley et al. (2003) and Dachs and Bertoldi (2005).

Results and discussion

The measured molar heat capacity (C_p) data of γ -Fe₂SiO₄ are listed in Table 1 and plotted in Fig. 1. A C_p polynomial of the general form $C_p = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3} + k_4 T + k_5 T^2 + k_6 T^3$ was used to fit the measured molar C_p data, which were split into several temperature regions due to the λ -anomaly. The C_p data below 5 K were estimated from a plot of C_p/T versus T^2 and a linear extrapolation to 0 K. The entropy of γ -Fe₂SiO₄ at STP is calculated from analytical and stepwise integration of the smoothed C_p data and was found to be identical within error when calculated by numerical integration. The resulting entropy value is 140.2 ± 0.4 J mol⁻¹ K⁻¹ (error is two standard deviations). The uncertainty in the entropy is estimated as described by Dachs and Geiger (2006).

In comparison with the C_p data of fayalite (Fig. 2, triangles), which has a very sharp λ -transition at 64.9 K as well as a small rounded hump near 16 K (Robie et al. 1982), the C_p data of γ -Fe₂SiO₄ (Fig. 2, circles) exhibit a broad maximum (λ -transition) at 11.8 K and a weak shoulder around 7 K, possibly related to a Schottky-anomaly (e.g., Gopal 1966) arising from the Fe²⁺ 3d orbitals. The broad λ -transition is likely due to a paramagnetic–antiferromagnetic transition just as the 65 K transition in fayalite (Santoro et al. 1966;

Table 1 Measured heat capacity data of γ -Fe₂SiO₄

514 1.83 49.88 17.83 12.06 13.181 14.34 77.03 514 1.856 50.03 17.53 12.06 13.204 143.43 77.17 514 1.852 53.56 18.96 12.27 13.042 148.57 74.81 551 2.230 57.41 20.83 12.29 13.059 153.6 77.38 5.9 2.865 57.47 20.87 12.51 12.893 153.69 77.34 5.91 2.885 61.53 2.295 12.71 12.893 153.69 77.34 5.23 3.501 61.61 2.293 12.74 12.70 138.88 79.71 6.32 3.621 6.505 2.541 12.74 12.70 163.50 82.21 6.77 4.424 6.507 2.541 12.74 12.72 163.50 82.17 7.22 5.248 70.71 2.812 13.99 12.287 106.44 84.6	T (K)	$C_{\rm p} (\mathrm{J} \mathrm{\ mol}^{-1} \mathrm{\ K}^{-1})$	<i>T</i> (K)	$C_{\rm p} (\mathrm{J} \mathrm{\ mol}^{-1} \mathrm{\ K}^{-1})$	<i>T</i> (K)	$C_{\rm p} (\mathrm{J} \mathrm{\ mol}^{-1} \mathrm{\ K}^{-1})$	T (K)	$C_{\rm p} ({\rm J \ mol^{-1} \ K^{-1}})$
5.14 1.852 50.35 18.97 12.06 13.204 148.5 74.54 5.51 2.280 53.56 18.96 12.27 13.072 148.57 74.81 5.51 2.286 53.62 19.04 12.28 13.064 148.57 74.88 5.51 2.286 57.741 20.84 12.29 13.069 133.68 77.28 5.9 2.885 67.741 20.84 12.51 12.893 153.68 77.34 5.91 2.885 61.33 2.298 12.71 12.7 138.88 79.71 6.32 3.6391 61.61 2.291 12.74 12.70 138.88 79.71 6.33 3.641 6.607 2.544 12.97 12.497 16.108 82.27 6.77 4.458 70.71 22.44 12.97 12.497 16.104 84.61 7.22 5.248 70.79 2.828 13.19 12.287 169.14 84.61 7.22 5.248 70.79 2.828 13.19 12.2087 169.14 <td>5.14</td> <td>1.863</td> <td>49.98</td> <td>17.48</td> <td>12.05</td> <td>13.181</td> <td>143.42</td> <td>72.03</td>	5.14	1.863	49.98	17.48	12.05	13.181	143.42	72.03
5.14 1.852 53.56 18.97 12.06 13.204 148.57 74.81 5.51 2.280 53.56 18.96 12.27 13.061 148.57 74.88 5.51 2.230 57.41 20.83 12.29 13.069 133.6 77.38 5.9 2.865 57.41 20.87 12.51 12.893 133.69 77.34 5.21 2.385 61.53 2.295 12.71 12.803 153.68 77.34 6.32 3.588 61.63 2.295 12.74 12.70 138.88 79.71 6.32 3.601 61.64 2.541 12.74 12.70 138.88 79.71 6.32 3.621 66.55 2.541 12.74 12.70 14.405 82.27 6.77 4.424 65.97 2.541 12.97 12.489 190.40 84.60 7.22 5.248 70.79 2.82.38 13.19 12.287 190.14 84.61 7.22 5.248 70.78 31.27 13.14 12.09 194.38	5.14	1.856	50.03	17.53	12.06	13.192	143.43	71.97
551 2.289 53.60 19.04 12.28 13.072 148.57 74.81 551 2.286 53.62 19.04 12.28 13.064 148.57 74.88 5.9 2.855 57.41 20.84 12.59 12.897 153.68 77.38 5.9 2.855 57.41 20.84 12.51 12.897 153.68 77.34 5.91 2.885 61.53 22.98 12.51 12.893 153.68 77.34 6.32 3.591 61.61 22.93 12.74 12.702 158.88 79.71 6.32 3.621 65.97 23.64 12.970 12.489 169.06 82.21 6.77 4.424 66.04 25.54 12.971 12.489 169.06 84.59 7.22 52.34 70.77 28.12 13.19 12.287 169.16 82.21 7.24 57.87 31.31 13.19 12.292 174.27 87.38 7.74 6.117 75.78 31.27 13.41 12.09 174.35 87.3 7.74 6.117 75.78 31.24 13.42 12.086 179.37 89.43 8.29 6.992 86.98 38.55 13.65 11.896 179.37 89.43 8.29 6.992 86.98 38.55 13.65 11.896 179.37 89.43 8.29 6.992 86.98 38.55 13.65 11.896 179.47 $98.$	5.14	1.852	53.56	18.97	12.06	13.204	148.5	74.54
5.51 2.286 57.41 20.483 12.29 13.069 13.36 77.38 5.9 2.855 57.41 20.483 12.29 13.069 73.36 77.38 5.9 2.855 57.47 20.487 12.51 12.893 133.69 77.34 5.21 2.885 61.53 22.95 12.73 12.71 158.88 79.78 6.32 3.588 61.53 22.95 12.74 12.77 158.88 79.78 6.32 3.621 65.95 25.41 12.74 12.77 163.96 82.21 6.77 4.424 65.97 22.54 12.97 12.497 1164.05 82.27 6.77 4.424 65.97 22.44 12.97 12.489 109.06 84.59 7.22 52.48 70.77 22.12 22.48 109.14 84.61 7.22 52.33 70.79 $22.52.3$ 13.10 12.292 174.27 87.38 7.74 6.144 75.78 31.27 13.41 12.06 174.35 87.44 7.74 6.117 77.38 31.27 13.41 12.066 179.37 89.45 7.74 6.117 77.38 35.01 13.42 12.466 179.37 89.45 7.74 6.117 77.38 35.01 13.42 12.666 179.37 89.45 7.74 6.117 87.37 83.55 13.66 11.996 179.47 89	5.51	2.289	53.56	18.96	12.27	13.072	148.57	74.81
5.91 2.865 57.41 20.84 12.5 12.897 153.68 77.38 5.91 2.865 57.47 20.87 12.51 12.893 153.68 77.34 5.91 2.865 57.47 20.87 12.51 12.893 153.68 77.34 6.32 3.588 61.53 22.95 12.73 12.74 153.68 79.71 6.32 3.591 61.61 22.93 12.74 12.70 163.96 82.21 6.77 4.424 65.97 25.36 12.96 12.35 164.04 82.15 6.77 4.424 66.04 25.54 12.97 12.497 164.05 82.27 7.22 5.248 70.71 28.14 12.97 12.497 164.05 82.27 7.22 5.248 70.71 28.12 13.19 12.287 169.14 84.6 7.22 5.248 70.71 28.12 13.19 12.287 169.14 84.6 7.22 5.244 75.78 31.27 13.41 12.09 17.435 87.3 7.74 6.112 81.16 35.07 13.64 11.095 17.945 89.55 8.29 6.902 86.98 38.25 13.66 11.890 17.45 89.36 8.29 6.902 86.98 38.25 13.66 11.890 17.45 89.36 8.29 6.902 86.98 38.25 13.66 11.890 19.45 <td>5.51</td> <td>2.286</td> <td>53.62</td> <td>19.04</td> <td>12.28</td> <td>13.064</td> <td>148.57</td> <td>74.88</td>	5.51	2.286	53.62	19.04	12.28	13.064	148.57	74.88
5.92.855574120.8412.5112.89715.36977.285.912.86561.5322.9812.5112.893153.6977.346.323.58861.5322.9512.7312.7715.88879.716.323.59161.6122.9312.7412.70215.88879.716.323.62166.5925.54112.7412.70215.88879.716.774.42466.9725.3612.9612.5164.0482.156.774.42166.0425.5412.9712.497164.0582.276.725.24870.7128.1213.1912.287164.0482.157.225.24870.7928.2813.1912.287164.0482.737.746.14775.7831.2713.4112.09174.3587.347.746.11775.8531.2413.4212.086179.3587.447.746.11281.1635.0713.6411.896179.4589.558.296.98781.2435.1213.6511.896179.4589.558.296.98781.2435.1213.6511.896179.4589.558.296.98781.2435.1213.6511.896179.4589.558.296.98781.2435.1213.6511.896179.4589.558.296.98781.8485.513.6511.896 <td< td=""><td>5.51</td><td>2.303</td><td>57.41</td><td>20.83</td><td>12.29</td><td>13.059</td><td>153.6</td><td>77.38</td></td<>	5.51	2.303	57.41	20.83	12.29	13.059	153.6	77.38
5.9 2.865 57.47 20.87 12.51 12.893 15.80 77.34 6.32 3.588 61.53 22.98 12.51 12.890 15.88 79.71 6.32 3.591 61.61 22.93 12.74 12.70 15.88.88 79.74 6.32 3.591 61.61 62.93 12.74 12.70 15.88.88 79.71 6.32 3.591 61.61 62.93 12.74 12.70 15.406 82.21 6.77 4.424 66.04 25.54 12.97 12.480 160.06 84.59 7.22 5.234 70.71 28.12 13.19 12.287 169.14 84.61 7.22 5.235 70.79 28.28 13.19 12.292 17.435 87.3 7.74 6.117 75.88 31.27 13.41 12.00 17.435 87.3 7.74 6.112 81.16 35.01 13.42 12.086 17.937 89.43	5.9	2.855	57.41	20.84	12.5	12.897	153.68	77.28
5.91 2.885 61.53 2.295 12.74 12.87 158.88 79.71 6.32 3.591 61.61 2.295 12.74 12.70 158.88 79.71 6.32 3.621 65.95 25.34 12.74 12.70 158.88 79.71 6.77 4.424 65.97 25.36 12.96 12.5 164.04 82.21 6.77 4.428 70.71 28.12 13.19 12.497 164.05 82.27 6.72 5.253 70.79 28.12 13.19 12.287 164.04 84.61 7.22 5.248 75.78 31.21 13.41 12.09 174.35 87.34 7.74 6.117 75.85 31.24 13.42 12.086 179.45 89.35 8.29 6.987 81.16 35.07 13.64 11.896 179.45 89.35 8.29 6.987 81.16 35.07 13.64 11.896 179.45 89.35	5.9	2.865	57.47	20.87	12.51	12.893	153.69	77.34
6.32 3.588 61.53 22.95 12.73 12.77 15.888 79.78 6.32 3.521 66.95 25.41 12.74 12.70 15.808 79.71 6.32 3.621 66.96 25.36 12.96 12.47 12.497 16.404 82.15 6.77 4.421 66.04 25.54 12.97 12.489 160.06 82.27 7.74 4.648 70.71 28.14 12.97 12.489 160.16 82.15 7.22 5.254 70.79 28.12 13.19 12.287 169.14 84.6 7.22 5.254 75.78 31.31 13.19 12.292 174.35 87.3 7.74 6.117 75.88 31.27 13.41 12.09 174.35 87.3 7.74 6.112 81.16 35.07 13.64 19.06 179.45 89.35 8.29 6.987 81.24 35.65 11.896 179.45 89.36	5.91	2.885	61.53	22.98	12.51	12.889	158.8	79.71
6.32 3.621 6.595 22.541 12.74 12.702 18.888 9.71 6.77 4.424 65.97 22.54 12.96 12.5 164.04 82.21 6.77 4.421 66.04 25.54 12.97 12.497 164.05 82.27 6.77 4.421 66.04 25.54 12.97 12.499 160.06 84.59 7.22 5.248 70.71 28.12 13.19 12.288 160.14 84.61 7.22 5.233 70.79 28.28 13.19 12.287 174.35 87.3 7.74 6.147 75.78 31.27 13.41 12.09 174.35 87.3 7.74 6.117 75.85 31.27 13.41 12.087 179.45 89.35 8.29 6.987 81.24 35.12 13.64 11.005 179.45 89.35 8.29 6.992 86.98 38.55 13.87 11.716 184.66 91.05 8.88 7.97 87.07 38.58 13.38 11.713 184.66 91.05 8.88 7.927 93.21 42.28 13.38 11.713 184.66 91.65 8.88 7.927 93.21 42.28 13.38 11.713 184.66 91.05 8.88 7.927 93.21 42.28 13.38 11.713 184.66 91.05 8.88 7.917 87.07 8.58 13.38 11.716 189.82	6.32	3.588	61.53	22.95	12.73	12.7	158.88	79.78
6.32 3.621 6.595 25.41 12.74 12.7 16.396 82.21 6.77 4.421 66.04 22.54 12.97 12.497 164.05 82.27 6.77 4.421 66.04 22.54 12.97 12.497 164.05 82.27 7.22 5.234 70.71 28.12 13.19 12.288 160.14 84.61 7.22 5.234 70.79 28.28 13.19 12.287 104.14 84.61 7.22 5.234 75.78 31.27 13.41 12.109 174.35 87.3 7.74 6.117 75.85 31.24 13.42 12.086 179.37 89.43 8.29 6.087 81.16 35.01 13.42 12.086 179.45 89.55 8.29 6.992 86.98 38.55 13.65 11.896 179.45 89.36 8.88 7.977 93.21 42.28 13.88 11.713 184.66 91.65 8.88 7.927 93.21 42.28 13.88 11.714 189.74 93.76 9.52 8.984 93.21 42.41 14.11 11.56 189.82 93.63 9.52 8.994 93.31 42.41 14.11 11.56 189.82 93.63 9.52 8.994 93.31 42.41 14.11 11.56 189.82 93.63 9.52 8.994 93.21 42.81 14.43 11.436 199.92	6.32	3.591	61.61	22.93	12.74	12.702	158.88	79.71
6.77 4.424 6.697 2.556 12.96 12.5 164.04 82.15 6.77 4.458 70.7 28.14 12.97 12.489 160.06 84.59 7.22 5.248 70.71 28.12 13.19 12.288 160.14 84.61 7.22 5.233 70.79 28.28 13.19 12.287 160.14 84.61 7.22 5.233 70.79 28.28 13.19 12.287 174.35 87.3 7.74 6.144 75.78 31.27 13.41 12.09 174.35 87.3 7.74 6.117 75.85 31.27 13.42 12.086 179.37 89.43 8.29 6.987 81.24 35.12 13.64 11.005 179.45 89.35 8.29 6.987 81.24 35.12 13.64 11.806 179.45 89.35 8.29 6.992 86.98 38.53 13.65 11.893 184.57 91.87 8.88 7.977 83.28 13.28 11.716 184.66 91.05 8.88 7.927 93.21 42.28 13.88 11.713 184.66 91.65 8.88 7.927 93.21 42.24 14.11 11.566 189.82 93.51 9.52 8.984 93.23 42.41 14.11 11.565 194.99 96.22 10.2 10.342 100.01 46.7 14.33 11.439 194.99 96.2	6.32	3.621	65.95	25.41	12.74	12.7	163.96	82.21
6.77 4.421 66.04 25.54 12.97 12.497 164.05 82.27 7.22 5.248 70.71 28.12 13.19 12.288 160.06 84.59 7.22 5.253 70.70 28.28 13.19 12.288 160.14 84.61 7.22 5.234 75.78 31.31 13.19 12.292 174.27 87.38 7.74 6.144 75.78 31.27 13.41 12.097 174.36 87.44 7.74 6.117 75.85 31.24 13.42 12.086 179.45 89.25 8.29 6.087 81.16 35.07 13.64 11.005 179.45 89.25 8.29 6.987 81.24 35.12 13.65 11.896 179.45 89.36 8.88 7.977 93.21 42.28 13.88 11.713 184.66 91.65 8.88 7.977 93.21 42.28 13.88 11.714 189.74 93.76 9.52 8.984 93.31 42.41 14.11 11.56 189.82 93.63 9.52 8.994 93.31 42.41 14.11 11.56 189.82 93.63 9.52 8.994 93.31 42.41 14.11 11.56 189.82 93.63 9.52 8.994 93.31 42.41 14.11 11.56 189.82 93.63 9.52 8.994 93.22 6.67 14.32 11.436 199.9	6.77	4.424	65.97	25.36	12.96	12.5	164.04	82.15
6.77 4.458 70.7 28.14 12.97 12.489 109.06 84.59 722 5.248 70.79 28.28 13.19 12.287 109.14 84.61 7.22 5.253 70.79 28.28 13.19 12.287 109.14 84.61 7.22 5.284 75.78 31.21 13.41 12.09 174.25 87.3 7.74 6.117 75.85 31.24 13.42 12.087 174.36 87.44 8.29 6.987 81.16 35.07 13.64 11.905 179.45 89.36 8.29 6.992 86.98 38.55 13.65 11.893 184.57 91.87 8.88 7.976 86.98 38.58 13.87 11.716 184.66 91.95 8.88 7.977 87.07 38.88 13.88 11.713 184.86 91.65 8.88 7.917 87.07 38.88 13.88 11.713 184.86 91.65 9.52 8.984 93.22 42.17 14.11 11.564 189.82 93.63 9.52 8.94 93.31 42.41 14.11 11.565 194.99 96.31 10.2 10.342 10.001 46.77 14.32 11.436 194.98 96.22 10.2 10.342 10.001 46.77 14.32 11.436 194.98 96.22 10.2 10.342 100.01 46.77 14.32 11.350	6.77	4.421	66.04	25.54	12.97	12.497	164.05	82.27
7.22 5.248 70.71 28.12 13.19 12.288 10.14 84.61 7.22 5.253 70.79 28.28 13.19 12.292 174.27 87.38 7.74 6.114 75.78 31.27 13.41 12.09 174.35 87.3 7.74 6.117 75.85 31.27 13.41 12.09 174.35 87.3 7.74 6.117 75.85 31.24 13.42 12.086 179.37 89.43 8.29 7.005 81.16 35.01 13.42 12.086 179.45 89.55 8.29 6.992 86.98 38.55 13.65 11.896 179.45 89.55 8.88 7.976 81.24 35.12 13.65 11.896 179.45 89.55 8.88 7.977 93.21 42.28 13.88 11.714 189.74 93.76 8.58 93.22 42.17 14.11 11.564 189.82 93.63 9.52 8.994 93.21 42.41 14.11 11.564 194.99 96.622 10.2 10.39 99.92 46.61 14.32 11.436 194.98 96.22 10.2 10.356 107.09 50.84 14.55 11.314 200.14 98.32 10.2 10.356 107.09 50.84 14.55 11.326 200.14 98.32 10.2 10.356 107.09 50.84 14.56 11.321 20.53 100.17 <tr< td=""><td>6.77</td><td>4.458</td><td>70.7</td><td>28.14</td><td>12.97</td><td>12.489</td><td>169.06</td><td>84.59</td></tr<>	6.77	4.458	70.7	28.14	12.97	12.489	169.06	84.59
7.22 5.253 70.7928.2813.1912.287109.1484.67.72 5.284 75.7831.3113.1912.287104.1484.67.74 6.144 75.7831.2713.4112.09174.3587.37.74 6.117 75.8531.2413.4212.087174.3687.448.297.00581.1635.0713.4411.905179.4589.358.29 6.987 81.2435.1213.6511.893184.5791.878.887.97686.9838.5513.6511.893184.5791.878.887.91787.0738.5813.8511.713184.6691.958.887.91787.0738.5813.8811.713184.6691.659.528.99493.3142.4114.1111.564189.8293.639.529.0149.99246.8114.1111.565194.9996.0110.210.3399.99246.8114.1111.565194.8996.2210.210.34210.0146.714.3311.439194.9996.0110.210.34210.0146.714.3311.438200.6698.4910.210.34210.0146.714.3311.438200.6698.4210.210.34210.0146.714.3311.438200.6698.4210.210.34210.0145.6511.312 <td< td=""><td>7.22</td><td>5.248</td><td>70.71</td><td>28.12</td><td>13.19</td><td>12.288</td><td>169.14</td><td>84.61</td></td<>	7.22	5.248	70.71	28.12	13.19	12.288	169.14	84.61
7.225.28475.7831.3113.1912.292174.2787.387.746.11475.7831.2713.4112.09174.3587.37.746.11281.1635.0113.4212.086179.3789.438.297.00581.1635.0113.4212.086179.3789.438.296.98781.2435.1213.6511.896179.4589.558.887.93686.9838.5513.6511.893184.5791.878.887.93793.2142.2813.8811.713184.6691.658.887.92793.2142.2813.8811.714189.7493.519.528.99493.3142.4114.1111.56194.9996.2210.210.342100.0146.714.3311.435194.9996.6110.210.342100.0146.714.3311.436200.1698.2210.210.356107.0950.8414.5511.314200.1498.2210.9412.138107.1950.8414.5511.314200.1498.2210.9412.138107.1950.8414.5511.314200.1498.2210.9412.138107.1950.8114.7711.23205.3100.1711.7113.208114.8856.2111.47811.24205.3100.1711.7113.208114.8556.3315.22 </td <td>7.22</td> <td>5.253</td> <td>70.79</td> <td>28.28</td> <td>13.19</td> <td>12.287</td> <td>169.14</td> <td>84.6</td>	7.22	5.253	70.79	28.28	13.19	12.287	169.14	84.6
7.74 6.141 75.78 31.27 13.41 12.09 174.36 87.3 7.74 6.117 75.85 31.24 13.42 12.087 174.36 87.44 8.29 7.005 81.16 35.07 13.64 11.905 179.45 89.35 8.29 6.987 81.24 35.12 13.65 11.893 184.57 91.87 8.89 6.992 86.98 38.55 13.65 11.893 184.57 91.87 8.88 7.976 85.98 33.58 13.87 11.716 184.66 91.65 8.88 7.917 87.07 38.58 13.88 11.713 184.66 91.65 9.52 8.984 93.22 42.17 14.1 11.564 189.82 93.63 9.52 9.014 99.92 46.67 14.32 11.436 194.99 96.22 10.2 10.339 99.92 46.67 14.32 11.436 194.99 96.01 10.2 10.342 100.01 46.7 14.33 11.438 200.66 98.49 10.2 10.342 100.01 46.7 14.32 11.438 200.14 98.32 10.94 12.135 107.09 50.98 14.33 11.438 200.66 98.49 10.2 10.342 100.01 46.7 14.32 11.342 205.3 100.11 11.7 13.16 11.79 50.98 14.35 11.342 <	7.22	5.284	75.78	31.31	13.19	12.292	174.27	87.38
7.74 6.112 81.16 35.01 13.42 12.087 174.36 87.44 7.74 6.112 81.16 35.01 13.42 12.086 179.37 89.43 8.29 6.987 81.14 35.12 13.65 11.896 179.45 89.36 8.29 6.992 86.98 38.55 13.65 11.893 184.57 91.87 8.88 7.936 86.98 38.58 13.85 11.716 184.66 91.65 8.88 7.927 93.21 42.28 13.88 11.714 189.74 93.76 9.52 8.984 93.22 42.17 14.11 11.56 189.82 93.63 9.52 9.944 99.92 46.67 14.32 11.436 194.98 96.22 10.2 10.339 99.92 46.67 14.32 11.436 194.98 96.22 10.2 10.342 100.01 46.7 14.33 11.438 200.66 98.49 10.2 10.356 107.09 50.84 14.55 11.314 200.14 98.32 10.94 12.135 107.09 50.84 14.55 11.326 200.52 100.45 11.71 13.208 114.79 55.81 14.77 11.234 205.3 100.17 11.71 13.208 114.88 56.21 14.78 11.24 205.3 100.17 11.71 13.208 114.88 56.51 15.22 10	7.74	6.144	75.78	31.27	13.41	12.09	174.35	87.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7.74	6.117	75.85	31.24	13.42	12.087	174.36	87.44
8.297.00581.1635.0713.6411.905179.4589.35 8.29 6.98781.2435.1213.6511.896179.4589.36 8.29 6.99286.9838.5513.6511.893184.5791.87 8.88 7.93686.9838.5813.8711.716184.6691.95 8.88 7.92793.2142.2813.8811.713184.6691.65 9.52 8.98893.2242.1714.111.564189.8293.63 9.52 9.01499.9246.6714.3211.436194.9996.32 10.2 10.33999.9246.6714.3311.436194.9996.62 10.2 10.342100.0146.714.3311.438200.1498.32 10.2 10.356107.0950.9814.3311.438200.1498.32 10.94 12.135107.0950.8414.5511.324200.1498.32 10.94 12.138107.1950.0714.5611.324205.3100.17 11.71 13.206114.8956.2114.7811.24205.3100.17 11.71 13.206114.8556.5115.0111.151210.45101.72 12.53 12.86312.3160.9415.0111.151210.45101.72 12.55 12.86312.3160.9415.0111.167216.21103.91 12.55 12.863 </td <td>7.74</td> <td>6.112</td> <td>81.16</td> <td>35.01</td> <td>13.42</td> <td>12.086</td> <td>179.37</td> <td>89.43</td>	7.74	6.112	81.16	35.01	13.42	12.086	179.37	89.43
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	8.29	7.005	81.16	35.07	13.64	11.905	179.45	89.55
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8 29	6 987	81.24	35.12	13.61	11.896	179.45	89.36
8.887.93686.9838.5813.8711.716184.6691.95 8.88 7.91787.0738.5813.8811.714189.7493.76 9.52 8.98893.2242.1714.111.564189.8293.61 9.52 8.99493.3142.4114.1111.565194.996.38 9.52 9.01499.9246.6114.3211.436194.9896.22 10.2 10.33999.9246.6714.3211.436194.9896.22 10.2 10.342100.0146.714.3311.439194.9996.01 10.2 10.356107.0950.9814.3311.438200.1498.32 10.94 12.138107.1950.9814.5611.326200.1598.25 10.94 12.138107.1950.9814.5611.326200.1598.25 10.94 12.143114.7956.0714.5611.321205.22100.45 11.71 13.208114.8856.2114.7811.24205.3100.17 11.71 13.208114.8856.2114.7811.24205.3100.17 11.71 13.208123.0360.861511.151210.45101.72 12.55 12.863123.1360.9415.0111.16210.47101.89 12.55 12.863123.1360.9415.0111.16210.47101.72 12.55 12.87<	8 29	6 992	86.98	38.55	13.65	11.893	184 57	91.87
8.887.917 87.07 38.58 13.88 11.713 184.66 91.65 8.88 7.927 93.21 42.28 13.88 11.714 189.74 93.76 9.52 8.988 93.22 42.17 14.1 11.564 189.82 93.63 9.52 9.994 93.31 42.41 14.11 11.565 194.99 96.38 9.52 9.014 99.92 46.67 14.32 11.436 194.98 96.22 10.2 10.339 99.92 46.67 14.33 11.436 194.98 96.22 10.2 10.342 100.01 46.7 14.33 11.438 200.06 98.49 10.2 10.342 100.01 46.7 14.33 11.438 200.14 98.32 10.94 12.138 107.09 50.84 14.55 11.314 200.14 98.32 10.94 12.138 107.09 50.84 14.55 11.326 200.14 98.32 10.94 12.138 107.09 55.81 14.77 11.24 205.3 100.17 11.71 13.208 114.88 56.21 14.78 11.24 205.3 100.17 12.55 12.863 123.03 60.83 14.79 11.16 210.47 101.89 12.55 12.863 123.03 60.85 15 11.151 210.45 101.73 12.55 12.864 131.88 65.61 15.01 11	8.88	7.936	86.98	38.58	13.87	11.716	184.66	91.95
8.88 7.927 93.21 42.28 13.88 11.714 189.74 93.76 9.52 8.984 93.22 42.17 14.1 11.564 189.82 93.63 9.52 8.994 93.31 42.41 14.11 11.564 189.82 93.63 9.52 8.994 99.92 46.67 14.32 11.436 194.98 96.22 10.2 10.339 99.92 46.67 14.32 11.436 194.98 96.22 10.2 10.356 107.09 50.98 14.33 11.438 200.06 98.49 10.33 12.135 107.09 50.84 14.55 11.324 200.14 98.32 10.94 12.138 107.19 50.98 14.56 11.321 205.22 10.45 11.7 13.176 114.79 55.81 14.77 11.234 205.3 100.17 11.7 13.208 114.88 56.21 14.78 11.24 205.3 100.17 11.71 13.203 60.86 15 11.151 210.45 101.72 12.55 12.869 123.03 60.86 15 11.151 210.47 101.89 12.55 12.863 123.13 60.94 15.01 11.167 215.52 103.81 13.44 12.077 141.36 71.99 15.23 11.071 220.62 103.91 13.44 12.077 141.36 71.03 55.67 19.99 <td>8.88</td> <td>7.917</td> <td>87.07</td> <td>38.58</td> <td>13.88</td> <td>11.713</td> <td>184.66</td> <td>91.65</td>	8.88	7.917	87.07	38.58	13.88	11.713	184.66	91.65
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8.88	7 927	93.21	42.28	13.88	11 714	189 74	93.76
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9.52	8.988	93.22	42.17	14.1	11.564	189.82	93.51
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9.52	8.994	93.31	42.41	14.11	11.56	189.82	93.63
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9.52	9.014	99.92	46.81	14.11	11.565	194.9	96.38
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	10.2	10.339	99.92	46.67	14.32	11.436	194.98	96.22
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10.2	10.342	100.01	46.7	14.33	11.439	194.99	96.01
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10.2	10.356	107.09	50.98	14.33	11.438	200.06	98.49
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.93	12.135	107.09	50.84	14.55	11.314	200.14	98.32
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.94	12.138	107.19	50.98	14.56	11.326	200.15	98.25
11.713.176114.7955.8114.7711.234205.3100.1711.7113.208114.8856.2114.7811.24205.3100.1111.7113.211123.0360.8314.7911.238210.36101.7312.5312.869123.0360.861511.151210.45101.7212.5512.863123.1360.9415.0111.16210.47101.8912.5512.87131.8865.6115.0111.157215.52103.8213.4212.084131.8865.5315.2211.04215.62103.9113.4412.077141.3670.915.2311.071220.62105.614.3411.411141.4571.8150.617.74220.71105.6314.411.411151.5176.4750.617.73225.83107.5915.4211.082151.5176.3755.6719.85225.92107.4315.4311.081151.6176.3455.7619.99230.91109.1616.5311.009162.4181.7560.9222.62231.01109.5416.5311.014162.4981.7560.9222.62236.14111.717.7111.07718.6594.2866.0925.48236.24111.9217.7111.07718.6594.2571.2528.6241.39114.1918.9811.17186.65<	10.94	12.143	114.79	56.07	14.56	11.321	205.22	100.45
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11.7	13.176	114.79	55.81	14.77	11.234	205.3	100.17
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11.71	13.208	114.88	56.21	14.78	11.24	205.3	100.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11.71	13.211	123.03	60.83	14.79	11.238	210.36	101.73
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.53	12.869	123.03	60.86	15	11.151	210.45	101.72
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.55	12.863	123.13	60.94	15.01	11.16	210.47	101.89
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12.55	12.87	131.88	65.61	15.01	11.157	215.52	103.82
13.44 12.077 131.97 65.78 15.22 11.059 215.62 103.89 13.44 12.077 141.36 70.9 15.23 11.071 220.62 105.6 14.38 11.408 141.36 71.03 50.53 17.65 220.7 105.63 14.4 11.411 141.45 71.81 50.6 17.74 220.71 105.86 14.4 11.411 151.51 76.47 50.6 17.73 225.83 107.59 15.42 11.082 151.51 76.37 55.67 19.85 225.92 107.43 15.43 11.081 151.61 76.34 55.76 19.99 23.091 109.16 15.33 11.086 162.41 81.85 60.83 22.43 231 109.39 16.53 11.014 162.49 81.75 60.92 22.62 231.01 109.54 16.53 11.014 162.49 87.7 60.93 22.56 236.14 111.7 17.71 11.076 174.08 87.68 66 25.28 236.23 111.76 17.71 11.077 186.65 94.28 66.09 25.47 241.31 113.72 18.97 11.167 186.65 94.25 71.25 28.6 241.4 114 18.98 11.17 200.04 100.19 71.25 28.45 246.45 115.75 20.34 11.294 200.04 100.19 76.31	13.42	12.084	131.88	65.53	15.22	11.04	215.62	103.91
13.44 12.077 141.36 70.9 15.23 11.071 220.62 105.6 14.38 11.408 141.36 71.03 50.53 17.65 220.7 105.63 14.4 11.411 141.45 71.81 50.6 17.74 220.71 105.86 14.4 11.411 151.51 76.47 50.6 17.73 225.83 107.59 15.42 11.082 151.51 76.37 55.67 19.85 225.92 107.43 15.43 11.086 162.4 81.91 55.76 19.99 230.91 109.16 16.53 11.009 162.41 81.85 60.83 22.43 231 109.39 16.53 11.014 162.49 81.75 60.92 22.62 231.01 109.54 16.53 11.014 162.49 87.7 60.93 22.56 236.14 111.7 17.71 11.076 174.08 87.68 66 25.28 236.23 111.76 17.71 11.076 174.08 87.68 66.09 25.47 241.31 113.72 18.97 11.167 186.65 94.25 71.16 28.26 241.39 114.19 18.98 11.17 200.04 100.1 71.25 28.65 246.45 115.75 20.34 11.294 200.04 100.19 76.31 31.21 246.55 116.13	13.44	12.077	131.97	65.78	15.22	11.059	215.62	103.89
14.38 11.408 141.36 71.03 50.53 17.65 220.7 105.63 14.4 11.411 141.45 71.81 50.6 17.74 220.71 105.86 14.4 11.411 151.51 76.47 50.6 17.73 225.83 107.59 15.42 11.082 151.51 76.37 55.67 19.85 225.92 107.43 15.43 11.081 151.61 76.34 55.76 19.99 230.91 109.16 16.53 11.009 162.41 81.85 60.83 22.43 231 109.39 16.53 11.014 162.49 81.75 60.92 22.62 231.01 109.54 16.53 11.018 174.08 87.7 60.93 22.56 236.14 111.7 17.71 11.076 174.08 87.68 66 25.28 236.23 111.76 17.71 11.076 174.08 87.68 66.09 25.47 241.31 113.72 17.71 11.077 186.65 94.25 71.16 28.26 241.39 114.19 18.98 11.17 186.72 94.25 71.25 28.6 241.4 114 18.98 11.17 200.04 100.1 71.25 28.45 246.45 115.75 20.34 11.294 200.04 100.19 76.31 31.21 246.55 116.13	13.44	12.077	141.36	70.9	15.23	11.071	220.62	105.6
14.4 11.411 141.45 71.81 50.6 17.74 220.71 105.86 14.4 11.411 151.51 76.47 50.6 17.73 225.83 107.59 15.42 11.082 151.51 76.37 55.67 19.85 225.92 107.43 15.43 11.081 151.61 76.34 55.76 19.99 230.91 109.16 16.53 11.009 162.41 81.85 60.83 22.43 231 109.39 16.53 11.014 162.49 81.75 60.92 22.62 231.01 109.54 16.53 11.018 174.08 87.7 60.93 22.56 236.14 111.7 17.71 11.076 174.08 87.68 66 25.28 236.23 111.76 17.71 11.082 174.15 87.83 66.09 25.48 236.24 111.92 17.71 11.077 186.65 94.25 71.16 28.26 241.39 114.19 18.97 11.167 186.65 94.25 71.25 28.6 241.4 114 18.98 11.17 200.04 100.1 71.25 28.45 246.45 115.75 20.34 11.294 200.04 100.19 76.31 31.21 246.55 116.13	14.38	11.408	141.36	71.03	50.53	17.65	220.7	105.63
14.4 11.411 151.51 76.47 50.6 17.73 225.83 107.59 15.42 11.082 151.51 76.37 55.67 19.85 225.92 107.43 15.43 11.081 151.61 76.34 55.76 19.99 225.93 107.64 15.43 11.086 162.4 81.91 55.76 19.99 230.91 109.16 16.53 11.009 162.41 81.85 60.83 22.43 231 109.39 16.53 11.014 162.49 81.75 60.92 22.62 231.01 109.54 16.53 11.018 174.08 87.7 60.93 22.56 236.14 111.7 17.71 11.076 174.08 87.68 66 25.28 236.23 111.76 17.71 11.076 174.08 87.68 66.09 25.47 241.31 113.72 17.71 11.077 186.65 94.25 71.16 28.26 241.39 114.19 18.97 11.167 186.72 94.25 71.25 28.6 241.4 114 18.98 11.17 200.04 100.1 71.25 28.45 246.45 115.75 20.34 11.294 200.04 100.19 76.31 31.21 246.54 116.3	14.4	11.411	141.45	71.81	50.6	17.74	220.71	105.86
15.42 11.082 151.51 76.37 55.67 19.85 225.92 107.43 15.43 11.081 151.61 76.34 55.76 19.99 225.93 107.64 15.43 11.086 162.4 81.91 55.76 19.99 230.91 109.16 16.53 11.009 162.41 81.85 60.83 22.43 231 109.39 16.53 11.014 162.49 81.75 60.92 22.62 231.01 109.54 16.53 11.018 174.08 87.7 60.93 22.56 236.14 111.7 17.71 11.076 174.08 87.68 66 25.28 236.23 111.76 17.71 11.076 174.08 87.68 66.09 25.47 241.31 113.72 18.97 11.167 186.65 94.25 71.16 28.26 241.39 114.19 18.98 11.17 186.72 94.25 71.25 28.6 241.4 114 18.98 11.17 200.04 100.1 71.25 28.45 246.45 115.75 20.34 11.294 200.04 100.19 76.31 31.21 246.54 116.3	14.4	11.411	151.51	76.47	50.6	17.73	225.83	107.59
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15.42	11.082	151.51	76.37	55.67	19.85	225.92	107.43
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	15.43	11.081	151.61	76.34	55.76	19.99	225.93	107.64
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15.43	11.086	162.4	81.91	55.76	19.99	230.91	109.16
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16.53	11.009	162.41	81.85	60.83	22.43	231	109.39
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16.53	11.014	162.49	81.75	60.92	22.62	231.01	109.54
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16.53	11.018	174.08	87.7	60.93	22.56	236.14	111.7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	17.71	11.076	174.08	87.68	66	25.28	236.23	111.76
17.7111.077186.6594.2866.0925.47241.31113.7218.9711.167186.6594.2571.1628.26241.39114.1918.9811.17186.7294.2571.2528.6241.411418.9811.17200.04100.171.2528.45246.45115.7520.3411.294200.04100.1976.3131.21246.54116.320.3411.291200.09100.276.431.81246.55116.13	17.71	11.082	174.15	87.83	66.09	25.48	236.24	111.92
18.9711.167186.6594.2571.1628.26241.39114.1918.9811.17186.7294.2571.2528.6241.411418.9811.17200.04100.171.2528.45246.45115.7520.3411.294200.04100.1976.3131.21246.54116.320.3411.291200.09100.276.431.81246.55116.13	17.71	11.077	186.65	94.28	66.09	25.47	241.31	113.72
18.9811.17186.7294.2571.2528.6241.411418.9811.17200.04100.171.2528.45246.45115.7520.3411.294200.04100.1976.3131.21246.54116.320.3411.291200.09100.276.431.81246.55116.13	18.97	11.167	186.65	94.25	71.16	28.26	241.39	114.19
18.9811.17200.04100.171.2528.45246.45115.7520.3411.294200.04100.1976.3131.21246.54116.320.3411.291200.09100.276.431.81246.55116.13	18.98	11.17	186.72	94.25	71.25	28.6	241.4	114
20.34 11.294 200.04 100.19 76.31 31.21 246.54 116.3 20.34 11.291 200.09 100.2 76.4 31.81 246.55 116.13	18.98	11.17	200.04	100.1	71.25	28.45	246.45	115.75
20.34 11.291 200.09 100.2 76.4 31.81 246.55 116.13	20.34	11.294	200.04	100.19	76.31	31.21	246.54	116.3
	20.34	11.291	200.09	100.2	76.4	31.81	246.55	116.13

T (K)	$C_{\rm p} ({\rm J \ mol}^{-1} {\rm K}^{-1})$	T (K)	$C_{\rm p} ({\rm J \ mol}^{-1} {\rm K}^{-1})$	T (K)	$C_{\rm p} (\mathrm{J} \mathrm{\ mol}^{-1} \mathrm{\ K}^{-1})$	<i>T</i> (K)	$C_{\rm p} ({\rm J \ mol^{-1} \ K^{-1}})$
20.34	11.297	214.38	105.7	76.4	31.89	251.61	117.74
21.79	11.413	214.38	105.74	81.46	35.16	251.69	118.14
21.79	11.421	214.41	105.57	81.55	35.22	251.7	117.85
21.8	11.414	229.76	110.36	81.56	35.1	256.67	118.97
23.35	11.552	229.76	110.34	86.58	38.29	256.75	119.2
23.35	11.552	229.77	110.23	86.66	38.43	256.77	119.24
23.36	11.542	246.24	116.64	86.67	38.29	261.89	120.81
25.02	11.742	246.27	116.49	91.75	41.3	261.98	121.45
25.02	11.734	246.28	116.48	91.84	41.49	262.07	121.55
25.04	11.732	263.81	121.38	91.85	41.55	267.06	122.98
26.81	11.91	263.92	121.3	96.91	44.59	267.13	122.98
26.81	11.898	263.94	121.04	97	44.71	267.15	123.31
26.83	11.959	282.7	126.59	97	44.83	272.11	124.38
28.73	12.07	282.85	126.47	102.07	48.1	272.19	124.05
28.73	12.064	282.85	126.58	102.16	47.88	272.21	124.15
28.75	12.086	302.95	132.51	102.16	48.12	277.36	125.07
30.78	12.293	303.14	132.3	107.22	50.93	277.43	125.24
30.78	12.296	303.15	132.52	107.31	51.29	277.44	125.24
30.81	12.311			107.32	51.15	282.51	126.28
32.99	12.642			112.35	54.25	282.57	126.65
32.99	12.644	10.68	11.502	112.43	54.54	282.59	126.69
33.02	12.664	10.69	11.492	112.44	54.41	287.56	128.03
35.35	13.09	10.69	11.491	117.51	57.51	287.62	128.05
35.35	13.089	10.91	12.091	117.59	57.7	287.64	128.34
35.39	13.121	10.92	12.104	117.6	57.84	292.8	129.95
37.89	13.739	10.92	12.102	122.7	60.65	292.88	130.2
37.89	13.728	11.14	12.582	122.78	60.73	292.88	129.94
37.92	13.756	11.14	12.593	122.79	60.86	297.95	131.21
40.6	14.33	11.14	12.589	127.86	63.53	298.02	131.15
40.6	14.326	11.37	12.946	127.94	63.61	298.03	131.38
40.64	14.364	11.37	12.944	127.95	63.86	302.99	132.38
43.51	15.14	11.37	12.959	133.02	66.05	303.06	132.46
43.51	15.14	11.59	13.145	133.1	66.23	303.06	132.6
43.56	15.18	11.6	13.165	133.1	66.22		
46.63	16.2	11.6	13.152	138.14	69.07		
46.63	16.2	11.82	13.228	138.22	69.16		
46.68	16.25	11.83	13.233	138.22	69.02		
49.98	17.45	11.83	13.234	143.34	71.84		

Table 1 continued

Ehrenberg and Fuess 1993). The C_p of γ -Fe₂SiO₄ measured by PPMS is generally lower than that of fayalite (Robie et al. 1982) in the temperature range of 50–300 K (Fig. 2). However, the difference of $C_{\rm p}$ between the two polymorphs decreases with increasing temperature. As a result, the C_p data of γ -Fe₂SiO₄ and fayalite differ less than 1 J mol⁻¹ K⁻¹ at 300 K. If this trend continues to high temperatures, the entropy difference (ΔS) and enthalpy difference (ΔH) for the fayalite-y-Fe₂SiO₄ transition will approach constant values, which means the only cause that can change the slope of the transition boundary will be a difference in volume. However, this situation is not supported by the $C_{\rm p}$ data of fayalite and γ -Fe₂SiO₄ measured between 350 and 700 K by Watanabe (1982), who showed there is a 4–6 J mol⁻¹ K⁻¹ difference between the C_p values of these two phases in the range of 350-700 K. Unfortunately, the C_p of γ -Fe₂SiO₄ between 300 and

350 K has not yet been measured and the PPMS routinely measures the C_p data only in the range 2–303 K. Therefore a reasonable and precise fitting of C_p polynomial above 298 K cannot be undertaken until the discrepancy between the available DSC data and the result of this study is resolved. Until then, an accurate representation of the phase boundary for the fayalite– γ -Fe₂SiO₄ transition at high pressures and temperatures is cumbersome.

The entropy of γ -Fe₂SiO₄ at standard pressure and temperature (S°_{298}) calculated from integration of the $C_{\rm p}$ data in this study may be compared with estimates from previous studies. The available estimates of the S°_{298} of γ -Fe₂SiO₄ range from 134 to 146 J mol⁻¹ K⁻¹ (e.g., Fei and Saxena 1986; Fei et al. 1991; Fabrichnaya 1998; Jacobs et al. 2001; Jacobs and de Jong 2005). The S°_{298} value of γ -Fe₂SiO₄ calculated from the measured $C_{\rm p}$ data in this study, 140.2 \pm 0.4 J mol⁻¹ K⁻¹, in the



Fig. 1 Comparison of the heat capacity data of γ -Fe₂SiO₄ measured by PPMS (*circles*) with those measured by DSC (*crosses*)

midpoint of the range of estimates, will serve as a strong constraint and substantial improvement for the thermodynamic data base of the Fe₂SiO₄ system. The enthalpy of the fayalite– γ -Fe₂SiO₄ transition at standard pressure and temperature ($\Delta H^{\circ}_{tr,298}$) is given by Akaogi et al. (1989) as 6.6 ± 2.4 kJ mol⁻¹. The enthalpy of formation at 298 K ($\Delta H^{\circ}_{f,298}$) of fayalite from elements is given by Robie and Hemingway (1995) as –1,478.2 ± 1.3 kJ mol⁻¹. By combining these two studies, the $\Delta H^{\circ}_{f,298}$ of γ -Fe₂SiO₄ is calculated to be –1,471.6 ± 2.7 kJ mol⁻¹, which together with our new entropy value, results in the value of Gibbs free

Fig. 2 Comparison of heat capacity data of γ -Fe₂SiO₄ (*circles*) with fayalite (*triangles*)

energy at standard pressure and temperature $(\Delta G^{\circ}_{f,298})$, -1,369.3 ± 2.7 kJ mol⁻¹.

The fayalite– γ -Fe₂SiO₄ transition boundary at 298 K can be calculated using the equation defined as follows:

$$\Delta G(P, 298) = \Delta H^{\circ}_{\text{tr}, 298} - 298.15 \Delta S^{\circ}_{\text{tr}, 298} + \int_{0}^{P} \Delta V(P', 298) dP' = 0$$
(1)

where $\Delta H_{tr,298}^{\circ}$ and $\Delta S_{tr,298}^{\circ}$ are enthalpy and entropy changes, respectively, for the fayalite- γ -Fe₂SiO₄ transition at STP, and $\Delta V(P,298)$ is the volume change at pressure *P* and at 298 K. The pressure dependence of the molar volume was expressed by the Birch–Murnaghan equation of state:

$$P = \frac{3}{2} K_0 \left[\left(\frac{V^{\circ}}{V} \right)^{7/3} - \left(\frac{V^{\circ}}{V} \right)^{5/3} \right] \\ \times \left\{ 1 - \frac{3}{4} \left(4 - K_0' \right) \left[\left(\frac{V^{\circ}}{V} \right)^{2/3} - 1 \right] \right\}$$
(2)

where K_0 and K'_0 are the isothermal bulk modulus and its pressure derivative, respectively. The fayalite– γ -Fe₂SiO₄ transition at 298 K is calculated to be at 2.4 ± 0.6 GPa based on current thermodynamic data given in Table 2. The error of the calculated pressure mainly results from the uncertainties of measured enthalpy change of the transition (Akaogi et al. 1989), with a small contribution from the uncertainties of measured entropies of fayalite and γ -Fe₂SiO₄ by Robie et al. (1982) and this study, respectively.



Eavalite $-1.478.2 \pm 1.3^{b}$ 151 ± 0.2^{c} 46.28^{d} 134^{c} 4^{f} 2.66	Phase	$\check{H}_{f,298} ~({ m kJ}~{ m mol}^{-1})$	\mathring{S}_{298} (J mol ⁻¹ K ⁻¹)	$\mathring{V}_{298} \ (\text{cm}^3 \ \text{mol}^{-1})$	K_0 (GPa)	K'_0	$\alpha = a + bT + cT^{-2} (K^{-1})^{a}$		
Eavalite $-1.478.2 \pm 1.3^{b}$ 151 ± 0.2^{c} 46.28^{d} 134^{e} 4^{f} 2.66							$a \times 10^5$	$b \times 10^9$	$c \times 10$
γ -Fe ₂ SiO ₄ -1,471.6 $\pm 2.7^{\text{g}}$ 140.2 $\pm 0.4^{\text{h}}$ 42.04 ⁱ 197 ^j 4 ^f 2.455	ayalite Fe ₂ SiO4	$\begin{array}{c} -1,478.2 \pm 1.3^{b} \\ -1,471.6 \pm 2.7^{g} \end{array}$	$\begin{array}{l} 151 \pm 0.2^{c} \\ 140.2 \pm 0.4^{h} \end{array}$	46.28 ^d 42.04 ⁱ	134 ^e 197 ^j	$\begin{array}{c} 4^{\rm f} \\ 4^{\rm f} \end{array}$	2.66 2.455	8.736 3.591	-2.487 -3.703

Table 2 Thermodynamic properties used for phase boundary calculation

Fei and Saxena (1986)

Robie and Hemingway (1995)

^c Robie et al. (1982)

^d Akimoto et al. (1976)

^e Kudoh and Takeda (1986)

^g Calculated from Akaogi et al. (1989)

^h This study

ⁱ Marumo et al. (1977)

^j Sato (1977)

The slope of the fayalite $-\gamma$ -Fe₂SiO₄ transition at 298 K is also calculated using the Clausius-Clapeyron equation:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S(P, 298)}{\Delta V(P, 298)} \tag{3}$$

where the entropy values at high pressure are corrected with a second order approximation using thermal expansion data at 298 K (Table 2) in the following way:

$$S(P, 298) \simeq S_{298}^{\circ} - \Delta P \alpha V_{298}^{\circ}$$
 (4)

Substituting P = 2.4 GPa into Eqs. 2–4, the slope of the fayalite-y-Fe₂SiO₄ transition at 298 K is calculated to be 25.4 bars/K.

Experimental determinations of the favalite-y-Fe₂SiO₄ transition are plotted and extrapolated to 298 K for comparison with our calculated phase boundary location at 298 K in Fig. 3. Even though most of these experiments were undertaken at high temperatures, between 1,000 and 1,500 K, the extrapolated locations of the transition boundaries by Akimoto et al. (1967) and Yagi et al. (1987) at 298 K agree with our calculation within 0.4 GPa whereas the extrapolated position of the transition by Akimoto et al. (1977) lies at higher pressure. Moreover, the calculated slope of the fayalite $-\gamma$ -Fe₂SiO₄ transition, 25.4 bars/K, is in excellent agreement with these experimental studies (Fig. 3), where the slope was given by either 25 bars/K (Akimoto et al. 1977; Yagi et al. 1987) or 26 bars/K (Akomoto et al. 1967). Because of the missing C_p data of γ -Fe₂SiO₄ between 300 and 350 K, a precise calculation of the phase



Fig. 3 Comparison of the phase transition boundary at 298 K calculated in this study with previous experimental studies. Black square represents our calculated location of phase transition boundary with two standard deviations. The calculated slope at 298 K is also plotted for comparison. A67 Akimoto et al. (1967), A77 Akimoto et al. (1977), Y87 Yagi et al. (1987)

boundary above 298 K cannot be completed at present.

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f Assumed

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