

Table III. Parameters of Equations 1, 2, and 3 and Standard Deviations

| | nonanoate | | | |
|--|-----------|-------|-------|---------|
| | Na | K | Rb | Cs |
| φ_v^0 , mL/mol | 168 | 170 | 180 | (182) |
| S_v , ($10^{3/2}$ mL ^{3/2} mol ^{-3/2}) | 2.53 | 3.76 | 0.94 | (3.46) |
| σ | 0.2 | 0.4 | 0.6 | (0.2) |
| $10^6\gamma$, bar ⁻¹ | 65.8 | 65.5 | 65.8 | (65.6) |
| $10^6\delta$, (bar M) ⁻¹ | 3.24 | 3.75 | 6.45 | (5.55) |
| σ | 0.1 | 0.08 | 0.08 | (0.07) |
| λ , cP M ⁻¹ | 8.61 | 11.80 | 11.83 | (12.84) |
| σ | 0.06 | 0.10 | 0.09 | (0.07) |

previously proposed for the higher homologues (2), $S_{f(\text{odd})} = 2.56n - 9.64$; from this equation in fact a value of $S_f = 13.4$ eu may be calculated.

Density, Compressibility, and Viscosity. The density values and the apparent molar volumes derived from the equation $\varphi_v = 10^3(d^0 - d)/mdd^0 + M_2/d(9)$, the compressibility, and the viscosity data are given in Table II, whereas in Table III are given the parameters of the following equations

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} \quad (1)$$

$$\beta_s = \gamma - \delta C \quad (2)$$

$$\eta = \eta^0 + \lambda C \quad (3)$$

that fit the experimental data; η^0 is given in Table I. Parameter A of the Jones-Dole equation (8), $\eta/\eta^0 = 1 + AC^{1/2} + BC$, is ≈ 0 in the limits of experimental error. From Table III it is evident that the dependence of η/C or β_s/C is more important in solutions with higher cation soaps, generally. Under the assumption that the salts are completely dissociated, the Glueckauf method (7), slightly modified as previously reported (1), may be employed in order to obtain φ_v^+ and φ_v^- . The φ_v^0 values concerning Na, K, and Rb soaps (more reliable owing to the high number of experimental measurements) expressed in the form

$$\varphi_v^0 = (4/3)\pi r^3 N + Kr^2 - A'z^2/r + \varphi_v^- \quad (4)$$

give the following values: $A' = 40 (\pm 5)$ (mL/mol) Å; $K = 11$

(± 2) mL/(mol Å²); $\varphi_v^- = 174 (\pm 2)$ mL/mol. The low values of φ_v^+ obtained from the additivity rule (-6 , Na⁺; -4 , K⁺; 6 , Rb⁺; 8 , Cs⁺) may be ascribed to the high value of the electrostriction constant. It is noteworthy that $\varphi_v^- \approx V_{\text{nonanoic acid}}$.

Glossary

| | |
|-----------------------|--|
| φ_v | apparent molar volume of the solute, the symbols 0, +, - have the following meaning, respectively: at infinite dilution, of the cation, of the anion, mL/mol |
| β_s | adiabatic compressibility, β^0 is of the pure solvent, bar ⁻¹ |
| u | ultrasonic velocity |
| d | density, d^0 is density of pure solvent, g/mL |
| η | viscosity, cP |
| m | molality |
| C | molarity |
| M | molecular weight of the solvent |
| M_2 | molecular weight of the solute |
| N | Avogadro's number |
| n | number of carbon atoms in the molecule |
| k | cryoscopic constant |
| ΔT | cryoscopic lowering |
| H_f | fusion enthalpy |
| S_f | fusion entropy |
| T_0, T_{fus} | fusion temperature of nonanoic acid |
| S_v | slope of the Masson equation |
| σ | standard deviation |

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Low-Temperature Heat Capacities of Potassium Disilicate

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Low-temperature heat capacities of crystalline potassium disilicate, $K_2Si_2O_5(c)$, were measured over the range 5–308 K by adiabatic calorimetry. The entropy, S^0 at 298.15 K, was calculated to be 45.55 ± 0.05 cal K⁻¹ mol⁻¹. The heat capacity, C_p^0 , entropy, S^0 , and Gibbs energy function, $(G^0 - H_0^0)/T$, are tabulated over the temperature range investigated. The heat capacity curve showed a normal sigmoid shape.

One of the Bureau of Mines overall goals is to maintain an adequate supply of minerals to meet national economic and strategic needs. Part of this effort involves supplying ther-

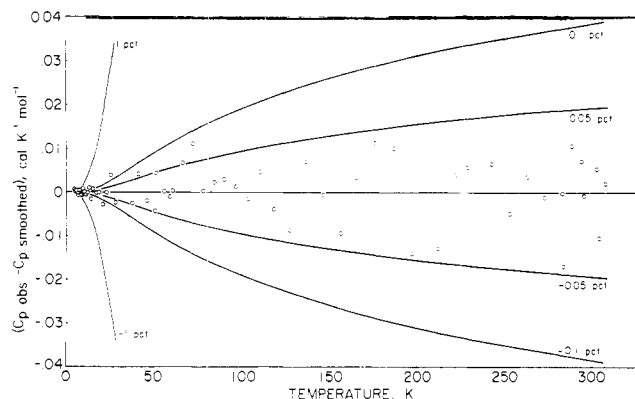
modynamic data on compounds of mineral and metallurgical interest, such as potassium disilicate. The heat capacities of potassium disilicate, $K_2Si_2O_5(c)$, were measured over the range of 5–308 K by adiabatic calorimetry. Related thermodynamic functions are tabulated over the range 5–300 K.

Materials and Apparatus

Crystalline potassium disilicate was prepared by reacting a mixture of reagent-grade potassium carbonate, K_2CO_3 , and silicic acid, $SiO_2 \cdot xH_2O$, in stoichiometric quantities of K_2O and SiO_2 . The reaction was initiated by heating the mixture in a platinum dish at 813 K for several hours, followed by a 5-day heating

Table I. Observed Heat Capacities of $K_2Si_2O_5(c)$

| T, K | $C_p^\circ, \text{cal K}^{-1} \text{mol}^{-1}$ | T, K | $C_p^\circ, \text{cal K}^{-1} \text{mol}^{-1}$ | T, K | $C_p^\circ, \text{cal K}^{-1} \text{mol}^{-1}$ |
|--------|--|--------|--|--------|--|
| 4.80 | 0.014 | 37.75 | 5.891 | 156.62 | 26.712 |
| 5.21 | 0.017 | 41.33 | 6.848 | 165.97 | 27.755 |
| 5.79 | 0.024 | 46.07 | 8.089 | 176.28 | 28.841 |
| 6.46 | 0.035 | 50.65 | 9.253 | 187.31 | 29.933 |
| 7.10 | 0.049 | 51.69 | 9.518 | 197.55 | 30.869 |
| 7.70 | 0.068 | 55.93 | 10.532 | 211.86 | 32.134 |
| 8.44 | 0.095 | 59.08 | 11.260 | 222.89 | 33.070 |
| 9.28 | 0.135 | 60.96 | 11.686 | 229.44 | 33.597 |
| 9.85 | 0.169 | 66.23 | 12.840 | 243.27 | 34.664 |
| 10.17 | 0.189 | 68.68 | 13.322 | 253.37 | 35.399 |
| 11.28 | 0.270 | 72.45 | 14.134 | 263.28 | 36.114 |
| 12.27 | 0.357 | 78.21 | 15.256 | 273.45 | 36.811 |
| 13.23 | 0.456 | 84.88 | 16.506 | 283.64 | 37.487 |
| 14.21 | 0.568 | 90.56 | 17.517 | 283.83 | 37.482 |
| 15.45 | 0.736 | 96.95 | 18.601 | 288.94 | 37.838 |
| 17.09 | 0.989 | 104.02 | 19.739 | 294.09 | 38.160 |
| 18.73 | 1.272 | 110.73 | 20.775 | 295.85 | 38.262 |
| 20.71 | 1.648 | 118.70 | 21.928 | 302.78 | 38.700 |
| 23.05 | 2.145 | 127.78 | 23.173 | 304.26 | 38.776 |
| 25.68 | 2.760 | 137.12 | 24.402 | 308.08 | 39.029 |
| 28.43 | 3.437 | 146.97 | 25.602 | | |

Figure 1. Deviations of observed heat capacities from smoothed values of $K_2Si_2O_5(c)$.

period at 1073 K. After the reaction was completed, the sample was ground and blended in an argon atmosphere and then heated at 1189 K for 19 h. The procedure was repeated twice, with a heating period each time of 6 days. The sample was ground and blended one final time and then analyzed. The X-ray analysis was in good agreement with the ASTM pattern for $K_2Si_2O_5(c)$. Optical microscopic examination indicated the material was crystalline and single phase, with an index of refraction of 1.50. This is in agreement with Kracek (2). Chemical analysis showed an average K_2O content of 43.93 wt % and a SiO_2 average of 56.16 wt % for a mole ratio of 1:2.004. Emission spectrographic analysis showed no significant metallic impurities. The molecular weight was calculated as 214.365 (1).

The details of construction of the adiabatic calorimeter and the method of operation have been reported elsewhere (3).

Results and Discussion

Experimental heat capacity data are listed in Table I. The overall uncertainty of the heat capacities was estimated to be

Table II. Thermodynamic Properties of $K_2Si_2O_5(c)$

| T, K | $\text{cal K}^{-1} \text{mol}^{-1}$ | | | |
|--------|-------------------------------------|-----------|----------------------------|--|
| | C_p° | S° | $-(G^\circ - H_0^\circ)/T$ | $H^\circ - H_0^\circ, \text{cal mol}^{-1}$ |
| 5 | 0.015 | 0.005 | 0.001 | 0.019 |
| 10 | 0.178 | 0.050 | 0.011 | 0.387 |
| 15 | 0.673 | 0.204 | 0.047 | 2.362 |
| 20 | 1.510 | 0.505 | 0.120 | 7.701 |
| 25 | 2.593 | 0.954 | 0.239 | 17.870 |
| 30 | 3.843 | 1.536 | 0.406 | 33.914 |
| 35 | 5.163 | 2.227 | 0.615 | 56.42 |
| 40 | 6.492 | 3.003 | 0.864 | 85.56 |
| 45 | 7.812 | 3.844 | 1.148 | 121.32 |
| 50 | 9.096 | 4.734 | 1.462 | 163.61 |
| 60 | 11.468 | 6.606 | 2.162 | 266.64 |
| 70 | 13.624 | 8.538 | 2.934 | 392.26 |
| 80 | 15.60 | 10.488 | 3.757 | 538.5 |
| 90 | 17.42 | 12.432 | 4.613 | 703.7 |
| 100 | 19.10 | 14.355 | 5.491 | 886.4 |
| 110 | 20.66 | 16.25 | 6.384 | 1085.3 |
| 120 | 22.12 | 18.11 | 7.283 | 1299.3 |
| 130 | 23.48 | 19.94 | 8.192 | 1527.3 |
| 140 | 24.76 | 21.72 | 9.088 | 1768.5 |
| 150 | 25.96 | 23.47 | 9.989 | 2022.2 |
| 160 | 27.10 | 25.18 | 10.883 | 2287.5 |
| 170 | 28.18 | 26.86 | 11.778 | 2564.0 |
| 180 | 29.21 | 28.50 | 12.661 | 2851.0 |
| 190 | 30.18 | 30.11 | 13.542 | 3147.9 |
| 200 | 31.11 | 31.68 | 14.408 | 3454.4 |
| 210 | 31.99 | 33.22 | 15.27 | 3769.9 |
| 220 | 32.83 | 34.72 | 16.11 | 4094.0 |
| 230 | 33.64 | 36.20 | 16.95 | 4426.4 |
| 240 | 34.41 | 37.65 | 17.79 | 4766.6 |
| 250 | 35.16 | 39.07 | 18.61 | 5114 |
| 260 | 35.88 | 40.46 | 19.42 | 5470 |
| 270 | 36.58 | 41.83 | 20.23 | 5832 |
| 273.15 | 36.79 | 42.25 | 20.47 | 5948 |
| 280 | 37.25 | 43.17 | 21.02 | 6201 |
| 290 | 37.90 | 44.49 | 21.81 | 6577 |
| 298.15 | 38.41 | 45.55 | 22.45 | 6888 |
| 300 | 38.52 | 45.79 | 22.59 | 6959 |

$\pm 1\%$ below 25 K, $\pm 0.5\%$ for 25–50 K, and $\pm 0.2\%$ for 50–310 K. Listed in Table II are the smoothed heat capacities and related functions given at convenient temperature intervals. The entropy, enthalpy, and Gibbs energy were determined below 5 K by smoothly extrapolating a plot of C_p/T vs. T^2 to 0 K. Deviations of the experimental heat capacities from the smoothed values are shown in Figure 1. Energy units of the tabular data are the defined thermochemical calorie (1 cal = 4.184 J). No other low-temperature data on $K_2Si_2O_5(c)$ were found in the literature.

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