the towers (a minimum distance of 8 km in our tests). In hilly terrain it is difficult to identify the cooling towers as the source, and a ground observer would probably assume that the snow was natural. Third, during the 3-year study of all of the AEP power plants with natural-draft towers and seven plants without cooling towers, no smoke plume alone was observed to produce snow or rain when it combined or merged with a natural cloud deck. Finally, the artificial snowfall often occurs when the atmosphere is cloudy and snow would be expected. In our tests, natural snow often coincided with tower-induced snow or occurred soon afterward.

However, the observations made during the winter of 1975–1976 are not unique. A similar snowfall was observed at Oak Ridge, Tennessee, in 1960 (*2*). The water vapor released from clusters of mechanical draft towers at the gaseous diffusion plant at Oak Ridge approximated that from a large power plant, and the weather conditions were similar to those which induced snow in our observations. Agee (*3*) has also described the artificial inducement of snowfall, but the incident he described appears to have been caused by a seeding effect of particles in supercooled fog. In Hanna and Gifford's recent comprehensive review of the possible meteorological effects of energy parks (*4*), there is no mention of snowfall.

It is too early to assess the environmental importance of the induced snowfall. With power plants in the size range and area studied, the effects seem likely to be minor. Occasional very small additions to natural snow and slight restrictions of visibility are all that one would anticipate. The effects of possible artificial snow must be carefully considered, however, when several large plants are to be clustered together, especially in cold climates.

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References

1. M. L. Kramer, M. E. Smith, M. J. Butler, D. E. Seymour, T. T. Frankenberg, *J. Air Pollut. Control Assoc.* **26**, 582 (1976); P. T. Brennan, D. E. Seymour, M. J. Butler, M. E. Smith, T. T. Frankenberg, *Atmos. Environ.* **10**, 425 (1976).
2. W. M. Culkowski, *Mon. Weather Rev.* **194**, 194 (1962).
3. A. M. Agee, *Bull. Am. Meteorol. Soc.* **52**, 557 (1971).
4. S. R. Hanna and F. A. Gifford, *ibid.* **56**, 1069 (1975).

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Entropy Estimates for Some Silicates at 298°K from Molar Volumes

Abstract. *Third law entropies for silicates of Be, Mg, Ca, Zn, Na, and K containing the same anion group, for example, SiO_4 or SiO_3 or $AlSi_3O_8$, are found to be linearly related to their molar volumes. The relationship between the molar volume and the entropy of silicates of Fe and Mn, atoms with unfilled* d *electron subshells, is different from that of other silicates. The linear correlations yield a useful method of estimating the entropies of ortho-, meta-, and framework silicates (feldspars and feldspathoids). The estimated entropies of pyrope and almandine at 298°K are 47.47 and 68.13 gibbs per mole, respectively.*

In calculations of phase equilibria, in cases where the entropies of silicates are not known the sum of the entropies of the constituent oxides can be substituted (*1, 2*). For many silicates, however, there is a significant difference between the two values. My purpose in this report is to explore the relationship between the entropy and the molar volume of silicates and to find if one can estimate entropy closely by using an empirical entropy-volume relationship. Such estimated entropies may be useful if they are closer to the experimentally determined entropies than those obtained by the oxide summation method.

Table 1 shows the data on experimentally determined entropies and molar vol-

Table 1. Molar volumes and experimental and estimated entropies of anhydrous silicates.

Silicate	Formula	n	Experimental S (gibbs/mole)	V (cm³/mole)	Calculated S (gibbs/mole)	$S_{exp}-S_{calc}$ (gibbs/mole)	$S_{exp}-S_{oxides}$ (gibbs/mole)
Estimated for orthosilicates from Eq. 1, σ = 0.047 (excluding γ-Ca_2SiO_4)							
Phenacite	Be_2SiO_4	1	15.37	37.19	15.23	0.14	−1.25
Larnite	β-Ca_2SiO_4	1	30.50	51.60	30.17	0.33	1.62
Ca-olivine	γ-Ca_2SiO_4	1	28.80	59.11	37.95	−9.15	−0.08
Grossularite	$Ca_3Al_2Si_3O_{12}$	1/3	57.70	125.3	59.94	−2.25	−12.63
Merwinite	$Ca_3MgSi_2O_8$	1/2	60.50	104.40	61.58	−1.530	−4.54
Forsterite	Mg_2SiO_4	1	22.75	43.79	22.08	0.67	−.01
Willemite	Zn_2SiO_4	1	31.40	52.42	31.02	0.38	0.66
Estimated for metasilicates from Eq. 3, σ = 0.027							
Wollastonite	$CaSiO_3$	1	19.60	39.93	20.57	−0.97	0.22
Pseudo-wollastonite	$CaSiO_3$	1	20.90	40.08	20.65	0.25	1.08
Ca-Al pyroxene	$CaAlAlSiO_6$	1/2	34.60	63.50	32.24	2.36	3.04
Diopside	$CaMgSi_2O_6$	1/2	34.20	66.09	33.66	0.54	−1.50
Enstatite	$MgSiO_3$	1	16.22	31.47	15.97	0.25	−0.10
Jadeite	$NaAlSi_2O_6$	1/2	31.90	60.47	30.56	1.346	−2.94
Estimated for feldspars and feldspathoids from Eq. 5, σ = 0.014							
Microcline	$KAlSi_3O_8$	4/15	52.47	108.72	52.44	0.03	5.49
Sanidine	$KAlSi_3O_8$	4/15	56.94	109.05	57.05*	0.11	5.52*
Kaliophilite	$KAlSiO_4$	2/7	31.85	59.89	31.93	−0.08	4.63
Leucite	$KAlSi_2O_6$	3/11	44.05	88.39	43.94	0.11	6.95
Low albite	$NaAlSi_3O_8$	4/15	50.20	100.07	48.90	1.30	5.48
High albite	$NaAlSi_3O_8$	4/15	54.67	100.43	53.52*	1.15	5.48*
Nepheline	$NaAlSiO_4$	2/7	29.72	54.16	29.59	0.13	4.76

*Includes a configurational entropy of disorder of 4.47 gibbs/mole.

Table 2. Molar volumes and experimental and estimated entropies of hydrous silicates. Values are calculated from Eq. 6, where σ = 0.017.

Silicate	Formula	n	Experimental S (gibbs/mole)	V (cm³/mole)	Calculated S (gibbs/mole)	$S_{exp}-S_{calc}$ (gibbs/mole)	$S_{exp}-S_{oxides}$ (gibbs/mole
Paragonite	$NaAl_3Si_3O_{10}(OH)_2$	4/15	67.61	132.10	67.68	−0.07	0.03
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	4/15	69.00	140.71	71.42	−2.42	0.80
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	4/15	76.40	149.91	75.42	0.98	−0.58
Kaolinite	$Al_2Si_2O_5(OH)_4$	1/2	48.53	99.52	48.72	0.19	−4.77
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	1/8	131.19	272.92	140.52	−9.34	−9.73
Chrysotile	$Mg_3Si_2O_5(OH)_4$	1/2	52.9	108.50	52.62	0.28	−7.54
Anthophyllite	$Mg_7Si_8O_{22}(OH)_4$	1/8	133.62	264.47	136.86	−3.23	−11.86
F-phlogopite	$KMg_3AlSi_3O_{10}F_2$	4/15	75.90	146.37	74.44	1.46	
Talc	$Mg_3Si_4O_{10}(OH)_2$	1/4	62.34	136.25	70.17	−7.83	−7.18

umes of all the ortho- and metasilicates listed by Robie and Waldbaum (*3*) and Helgesson (*2*) except for the Al_2SiO_5 polymorphs, $ZrSiO_4$, and $CaMgSiO_4$. The entropy of $CaMgSiO_4$ listed in Robie and Waldbaum was not determined experimentally; $ZrSiO_4$ is the only silicate with a tetravalent cation. The relationship of Al_2SiO_5 to the other orthosilicates is complicated by the substitution of Al plus O for two divalent cations.

The relationship between the molar volumes and the entropies of orthosilicates of Be, Mg, Ca, and Zn including grossularite ($Ca_3Al_2Si_3O_{12}$) is given by

$$-23.3129 + 1.0365\,n\,V = n\,S \quad (1)$$

where n is one divided by the number of tetrahedrally coordinated ions in the silicate, V is the molar volume (in cubic centimeters per mole), and S is the entropy (in gibbs per mole) (1 gibbs = 1 cal/°K). Entropies estimated by the use of Eq. 1 have been listed in Table 1.

For orthosilicates containing the transition elements Mn and Fe, atoms with unfilled d subshells, Eq. 1 does not hold. (Unfortunately, data on such orthosilicates as Co_2SiO_4 and Ni_2SiO_4 are not available.) From the two data points on the orthosilicates of Mn and Fe we have

$$-38.7322 + 1.5991\,n\,V = n\,S \quad (2)$$

Equation 2 may be improved when more data are available on other orthosilicates with nonspherical ions. It has been included here because it yields an acceptable value of entropy for almandine ($Fe_3Al_2Si_3O_{12}$) as discussed below.

Relations similar to Eqs. 1 and 2 have been obtained for metasilicates. These are

$$-1.1508 + 0.5439\,n\,V = n\,S \quad (3)$$

for the metasilicates of Mg, Ca, and Na-Al and

$$-20.7522 + 1.2870\,n\,V = n\,S \quad (4)$$

for $FeSiO_3$ and $MnSiO_3$. For the metasilicates of transition elements, we have, as with the orthosilicates, only two data points: The entropy for $MnSiO_3$ is from Robie and Waldbaum (*3*), and the value for $FeSiO_3$ has been estimated by Saxena (*4*).

The entropy–molar volume relationship for feldspars and feldspathoids is

$$-2.1205 + 0.4092\,n\,V = nS\,(+\,2R\ln 2) \quad (5)$$

where R is 1.987 and $2R\ln 2$ is the disorder entropy. The value of n here is the total number of tetrahedrally coordinated cations divided by the total charge on such ions. For example, n for $KAlSi_3O_8$ is 4/15, where the numerator of the fraction represents the number of cations other than K and the denominator represents the sum of the charges.

A comparison of the entropy differences in Table 1 reveals that Eqs. 1, 3, and 5 generally yield better estimates of entropy than the oxide summation method. In particular, the entropies of grossularite, feldspars, and feldspathoids estimated by the method presented here are superior to those estimated by the oxide summation method. However, the entropy of γ-Ca_2SiO_4 calculated from the entropy-volume relationship is grossly erroneous.

The entropy–molar volume relationship for the hydrous silicates is given by

$$2.7468 + 0.4344\,n\,V = n\,S \quad (6)$$

Here n is defined as in Eq. 5. As the data in Table 2 show, this relationship is less useful than those for the anhydrous silicates.

Table 1 shows the standard deviations, σ, for the least-squares fit. It is difficult to determine a reasonable estimate of errors with the entropy-volume method because of uncertainties in the molar volumes and in the experimentally determined entropies.

Garnets are important rock-forming minerals in the deep crust and upper mantle. Therefore, a knowledge of the entropies of almandine ($Fe_3Al_2Si_3O_{12}$) and pyrope ($Mg_3Al_2Si_3O_{12}$) is essential to an understanding of the phase equilibrium relations and to the construction of models of evolution of the earth. The entropy-volume method may be used to estimate the entropies of pyrope and almandine. The molar volumes of these silicates are 113.27 and 115.27 cm³/mole, respectively. Using Eq. 1 for pyrope, we have $-23.3129 + 1.0365\ (113.27/3) = S/3 = 15.82$, or $S = 47.47$ gibbs/mole. The summation of the entropies of the constituent oxides for pyrope is 61.14 gibbs/mole. Considering the difference between the experimental entropy and the oxide sum entropy of grossularite (Table 1), the estimated entropy of pyrope appears to be of the right order. For almandine we have (from Eq. 2) $-38.7322 + 1.5991\ (115.27/3) = S/3 = 22.71$, or $S = 68.13$ gibbs/mole, which compares very well with the value of 68.3 ± 3 gibbs/mole calculated by Zen (*5*) using data on phase equilibria.

The results of these calculations indicate that the entropies of most anhydrous silicates can be estimated with accuracy with the use of these entropy-volume relationships. These relationships, however, depend upon the nature of the cations, and, although significant correlations have been found here for silicates of several ions, these relations must be used with caution for silicates of other ions.

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References

1. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions* (Prentice-Hall, Engelwood Cliffs, N.J., 1952); W. S. Fyfe, F. J. Turner, J. Verhoogen, *Geol. Soc. Am. Mem. 73* (1958).
2. H. C. Helgesson, *Am. J. Sci.* **267**, 729 (1969).
3. R. A. Robie and D. R. Waldbaum, *U.S. Geol. Surv. Bull.* **1259**, 256 (1968).
4. S. K. Saxena, unpublished data.
5. E-An Zen, *Contrib. Mineral. Petrol.* **39**, 65 (1973).

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A Hexagonal (Wurtzite) Form of Silicon

Abstract. *The existence of a hexagonal (wurtzite) form of silicon, similar to that form of diamond (carbon) observed in meteorites and in the laboratory, has been identified by x-ray diffraction in reaction-bonded silicon nitride containing unreacted silicon. The presence of this phase is due to stresses created in the silicon by the nitridation reaction.*

We prepared reaction-bonded silicon nitride (Si_3N_4) by maintaining a compacted volume of finely powdered (−200 mesh) silicon in a nitrogen atmosphere at temperatures between 1250° and 1500°C for several hours to several days. During an extensive microstructural characterization of this material, we used x-ray diffraction to check the relative amounts of α- and β-Si_3N_4, the extent of reaction, and the existence of any impurity compounds. We obtained powder patterns with $CuK\alpha$ radiation on a Nonius diffractometer using monochromatic radiation (graphite-focusing crystal); the intensity as a function of 2θ (where θ is the dispersion angle) was recorded between 12° and 72°. Unreacted silicon was always present and was used as a standard. All of the x-ray peaks expected for α- and β-Si_3N_4 and unreacted silicon (diamond cubic) were observed and easily identified by reference to the Joint Committee on Powder Diffraction Studies powder