

SUPPLEMENTARY MATERIAL

Deviations from the Best-Fit Line

In Figure 1, eight of the data points S° vs. ΔH° deviating most visibly from the best-fit line are labeled. Because data for the 26 monatomic solids in Table 1 (with $\Delta H^\circ < 7800 \text{ J/mol}$) are difficult to discern, data for monatomic solids, along with the (dashed) best-fit line, are shown separately in Figure 5. Also shown is the (solid) curve for S° vs. ΔH° predicted by the Debye theory for monatomic solids. We now discuss seven notable issues.

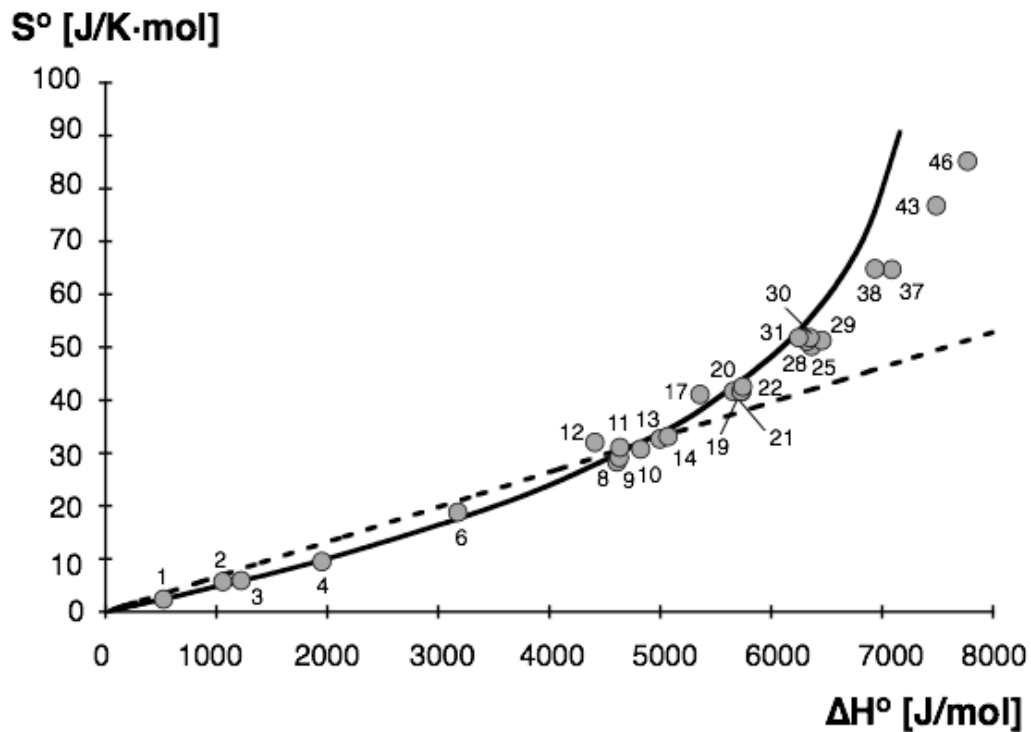


Figure 5. S° vs. ΔH° for the Debye model (solid curve) and empirical data for 26 monatomic solids. The dashed line is the best-fit line $S^\circ = 0.0066 \Delta H^\circ$ from Figure 1, and the numbers shown are substance numbers from Table 1. Note that the maximum molar heat capacity $\Delta H^\circ \approx 8000 \text{ JK}^{-1}\text{mol}^{-1}$, compared with the maximum of $\Delta H^\circ \approx 80000 \text{ JK}^{-1}\text{mol}^{-1}$ in Figure 1.

1. The solid curve in Figure 5 was generated using the Debye model of a monatomic solid to calculate $\Delta H^o = \Delta U^o$ (because neither pressure nor volume appear explicitly in the Debye model) and S^o for various values of the Debye temperature Θ_D . (37) On this curve, as ΔH^o increases, Θ_D decreases, and the standard entropy clearly increases as the Debye temperature decreases. Because Θ_D is proportional to the maximum frequency of the Debye model oscillators – and the higher frequencies dominate in the Debye model – we conclude that entropy is lowest for substances where the highest frequency vibrations dominate – e.g., diamond.

2. The Debye curve in Figure 5 and the triangle data set in Figure 1 are not consistent with eq 3, with substances lying below the best-fit line for the lowest values of ΔH^o and above it for the highest values. Given the impressive success of the Debye theory, we expect the Debye curve to be at least qualitatively correct, and we expect the fourteen solids with $\Delta H^o > 5300 \text{ J/mol}$ (#17, 19-22, 25, 28-31, 37-38, 43, 46) to lie above the best-fit line.

3. The latter fourteen solids have heat capacities that rise relatively rapidly with temperature and nearly reach their maximum classical value by $T = T^o = 298.15 \text{ K}$. Put differently, these substances have Debye temperatures below (many well below) T^o . The relatively high heat capacity for lower temperatures weights the distribution function $f(T)$, causing the average temperature $\langle T \rangle$ to be less than $T^o / 2$, which implies $S^o / \Delta H^o > 0.0066 \text{ K}^{-1}$; i.e. data points lying well above the best-fit line.

4. Solids #1-4, 6, 8-10 are well described by the Debye theory, and their data points near the Debye curve and below the best-fit line. Although the best-fit line appears in Figure 5 to lie "nearly on" data point #1 for diamond, it is actually 46% above that point. Similarly, it is 20.7% above #2 (graphite) and 36.7% above #3 (boron). Entropy values for these solids are extremely small (2.36 - 5.74 J K⁻¹mol⁻¹) compared with most other substances, and thus the large percentage differences are understandable.

5. Six solids – uranium (#25), sodium (#29), potassium (#37), lead (#38), rubidium (#43), and cesium (#46) – have entropy values that are significantly below the Debye curve for their ΔH° values. Each of these has one or more unusual properties. Cs, Rb, K, and Na have respective atomic radii 334, 298, 278, and 223 picometers (pm), i.e., among the largest for any elements. Furthermore, the respective melting temperatures of Cs, Rb, and K are 301.7 K, 312.8 K, and 336.5 K, near the standard temperature, 298.15 K. The other two elements Pb and U are considerably heavier than most other monatomic solids. We suspect that these properties are accompanied by non-negligible anharmonic forces. This would account for the deviations from the Debye theory, which is based solely on harmonic forces proportional to separation distance.

6. Figure 5 shows a pattern: The five lightest monatomic solids, with the smallest atoms, have entropy vs. enthalpy input data points that lie below the best-fit line. The 11 heaviest monatomic solids, with the largest atoms, lie above the best-fit line. Of course, this mass-related vibrational pattern does not hold for heavy polyatomic, covalent solids, as illustrated by eicosane, C₂₀H₄₂. Although it has the heaviest and largest molecular unit among the first 76 solids, the best-fit line in Figure 1 lies only 0.3% above eicosane's empirical data point. Clearly, the intra-molecular vibrations such as C-C and C-H bond bending are responsible for this. That is, a fictitious solid of rigid molecules with

eicosane's size and mass would be expected have its $(S^{\circ}, \Delta H^{\circ})$ data point near the Debye curve. However, the internal molecular vibrations result in the nearly linear heat capacity shown in Figure 4, which causes $(S^{\circ}, \Delta H^{\circ})$ for eicosane to be nearly on the best-fit line. This picture is supported by the fact that if monatomic solids are deleted from Figure 1, the best-fit line is still given by eq 3, but with a somewhat larger value of R^2 – i.e., an even greater linear correlation between S° and ΔH° .

7. The thermal behavior of solids is complex, depending upon crystal structure, degree of isotropy, size and composition of polyatomic units, atomic masses, force constants, and degree of anharmonicity. The patterns seen here, and our explanations, are intended to clarify some of the reasons why a substance's $(S^{\circ}, \Delta H^{\circ})$ point will be near or displaced from the best-fit line – even though we have only scratched the surface of the complex phenomena.