Cryogenic heat-capacity determinations provide a useful tool for the determination of the energetic spectrum of condensed phases and also reveal information on their discrete electronic level structures as well. We have been interested in applying these techniques to actinide elements and have in recent months been working up the techniques to unravel the corresponding data for the lanthanide compounds—where opposite trends in cationic masses and molar volumes provide an opportunity to test theories useful for the resolution of excess heat capacity from lattice contributions.

As an important aspect of heat capacities—especially of compounds with d and f electrons—the Schottky contribution deserves to be much better known—by chemists, by physicists, and by students of thermodynamics. These remarks are designed to further that goal.

Schottky’s “Orphaned” contribution

Werner Schottky first showed in 1922 [1] that a contribution to the energetics—spectroscopic or thermophysical—of a substance could be expected from excited electronic levels. The splitting of the ground-level term by the crystalline electric field also gives rise to the appearance of such a “Schottky anomaly” or “Schottky contribution” either in the heat capacity or in other thermophysical properties. The manifestation of this contribution to the heat capacity is a characteristic bell-shaped curve skewed out on the high-temperature side. The temperature of the peak is related to the energetic separation of the levels and the maximum height is determined by the ratio of the degeneracies. Moreover, the total entropy under the curve is also related to the number of levels and the degeneracies involved. When the electronic energy increments are sufficiently small, the Schottky anomaly occurs at so low a temperature that, in comparison to the lattice contribution, the Schottky contribution stands out clearly. When energy levels are sufficiently spread so as to cause the occurrence of the contribution near or above ambient temperature, the maximum is typically so spread out as to be unrecognized unless the heat capacities of isostructural substances with nearly identical atomic masses are used for
comparison. Nonetheless, the Schottky contribution does represent an important aspect of the morphology of the heat-capacity curves and tends to do so increasingly as higher temperatures are involved whenever one is dealing with transition-element, lanthanide-element, and actinide-element compounds.

Never again did he discuss the Schottky contribution. Schottky effects and Schottky defects occupied his career.

**Brief mathematical interlude**

The Schottky heat-capacity function, \( \text{Sch} (u) \), is rigorously related to an Einstein heat-capacity function, \( \text{Ein} (u) \), by both an additive and a multiplicative identity:

\[
\text{Ein} (u) - \text{Ein} (2u) = \text{Sch} (u) \quad \text{and} \quad \text{Ein} (u) \, \text{Sch} (u) = u^2 \, \text{Ein} (2u).
\]

These by no means exhaust the family of rigorous relationships, and in the course of considerable experimentation with the mathematics of these functions we have deduced about 40 equations to deal with two-level Schottky functions with equal degeneracies and—at the present time—with integral arguments. For the more difficult—and far more useful—cases of many levels, differing degeneracies, and non-integral arguments (which differ from each other by a per cent or so) we have been obliged to use—with somewhat less rigor—series approximations or numerical evaluation.

Some of my friends claim to find evidence for Schottky functions by differencing the heat capacities of a compound and its diamagnetic analog (utilized as a lattice contribution). In these instances the difference is indeed probably exactly a Schottky function, but it is occasioned simply by the fact that the Einstein or Debye thetas of the two substances differ slightly, and the apparent Schottky contribution is an artifact occasioned simply by the additive identity already presented. Moreover, the difference between the heat capacities of a vitreous phase and the corresponding crystal (e.g., \( B_2O_3 \)) is also—for somewhat the same reasons—a Schottky function.

**A byte on morphology**

The Schottky function is a beast that is a little hard to "fudge". Its shape is totally determined by the levels and the degeneracies. In the simple system already discussed, maximum height is independent of the temperature and is governed only by the degeneracies. In a system with more energy levels, the shape of the anomaly is determined, of course, by the overall pattern of energy levels. Calculations for the

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