

11.1: Heat Capacity as a Function of Temperature

It is relatively easy to measure heat capacities as a function of temperature. If we measure the constant-pressure heat capacity of a pure substance over a wide temperature range, we typically observe a curve like that in Figure 1. The heat capacity is a smooth, continuous function of temperature except for a small number of discontinuities. These occur at temperatures where the substance undergoes phase changes. These can be changes from one solid phase to another, melting to convert a solid phase to the liquid, or vaporization to convert the liquid to the gas. The details of the curve are pressure dependent; for example, at a low pressure, we might observe sublimation of the material from a solid phase directly into its gas phase.

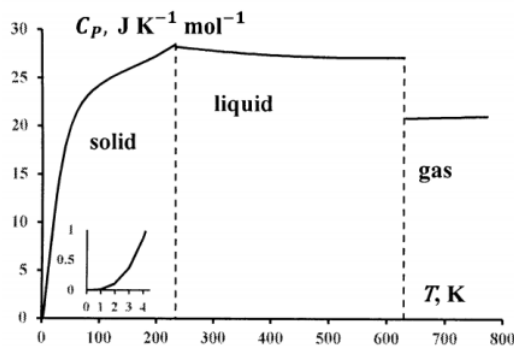


Figure 1. Heat capacity of mercury *versus* temperature

Another general feature of these curves is that the heat capacity of the solid substance decreases to zero as the absolute temperature decreases to zero; the curve meets the abscissa at the zero of temperature and does so asymptotically. That this is true for all substances seems like an odd sort of coincidence. Why should all solid substances exhibit essentially the same heat capacity (zero) at one temperature (absolute zero)?

As it turns out, this result has a straightforward molecular interpretation in the theory of statistical thermodynamics. In [Section 22.6](#), we consider a theory of low-temperature heat capacity developed by Einstein. Einstein's theory explains all of the qualitative features that are observed when we measure heat capacities at low temperatures, but its predictions are not quantitatively exact. Debye extended the Einstein model and developed a theory that gives generally excellent quantitative predictions. The Debye theory predicts that, at temperatures near absolute zero, the heat capacity varies as the cube of temperature: $C_P = AT^3$, where A is a constant. If we have heat capacity data down to a temperature near absolute zero, we can estimate the value of A from the value of C_P at the lowest available temperature.

Anticipating results that we develop in [Chapter 22](#), we can characterize the statistical interpretation as follows: When a system of molecules gives up heat to its surroundings, some of the molecules move from higher energy levels to lower ones. Statistical thermodynamics posits that the fraction of the molecules that are in the lowest energy level approaches one as the temperature goes to zero. If nearly all of the molecules are already in the lowest energy level, decreasing the temperature still further has a negligible effect on the energy and enthalpy of the system.

Given such heat capacity data, we can find the enthalpy or entropy change that occurs as we change the temperature of a quantity of the substance from some reference temperature to any other value. When we use pressure and temperature as the independent variables, we have

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

and

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

At constant pressure, we have

$$(dH)_P = C_P dT$$

so that

$$H(T) - H(T_{ref}) = \int_{T_{ref}}^T C_P dT$$

and

$$(dS)_P = \frac{C_P}{T} dT$$

so that

$$S(T) - S(T_{ref}) = \int_{T_{ref}}^T \frac{C_P}{T} dT$$

If phase transitions occur as the temperature goes from the reference temperature to the temperature of interest, these integrations must be carried out in steps. Also, we must include the enthalpy and entropy changes that occur during these phase changes.

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