

2.9 Experimental data on the heat capacity

Here we will state some very important and famous results related to heat capacity.

- Usually C is positive; famous exceptions are:
 - Metastable systems, e.g. clusters (energy dominated by surface).
 - Black holes. The absorption of mass increases its internal energy U , but the temperature T of a black hole is inversely proportional to its mass. Thus: the more mass a black hole absorbs, the colder it becomes, i.e. $C_V = \Delta U/\Delta T < 0$.
- Dulong and Petit (1819): $C_{p,m}(solid) = 3R = 24.9 \text{ J/K}$.
 - This is a good approximation for the metallic elements at high T (room temperature): C ranges from about $2.8 R$ to $3.4 R$ (cf. the extrapolation for large T in Figs. 2.5 a) and 2.6).
 - It can be explained by the excitation of $3N$ oscillations, every oscillation mode contributes with R .
 - Strong deviations are found at low T ; in this regime the T^3 -law of Debye holds, or the linear T -dependence (electrons in metals) is found (cf. Fig. 2.6).
 - Jumps in C_p/T at phase transitions show up (cf. Fig. 2.5 b)).
 - Smaller heat capacities are found for solids of light, tightly-bonded atoms such as beryllium ($2.0 R$) and diamond at only $0.735 R$ (cf. Fig. 2.5 a). The latter conditions create large quantum vibrational energy spacing, so that many vibrational modes are frozen out still at room temperature.
- Kopp (1865):
 - C_p of a solid/liquid is the sum of the atomic heat capacities of the elements composing it.
 - Elements having lower heat capacities (as expected by the Dulong and Petit law) retain these lower values even in their compounds
 - e.g. KCl: $C_{V,m} \approx 6R$, MgCl_2 : $C_{V,m} \approx 9R$.
 - Extension to slurries/solutions possible (composition average), e.g.

$$C_{p,m}(solution) = x_{water}C_{p,m}(water) + x_{salt}C_{p,m}(salt) \quad \text{where } x \text{ is the corresponding mole fraction} \quad (2.24)$$

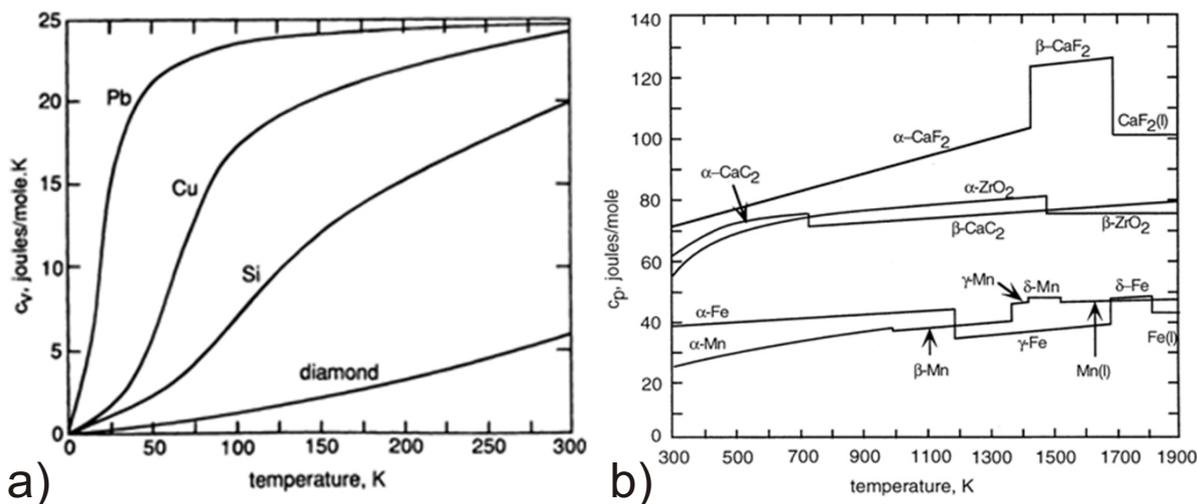


Figure 2.5: a) C_V vs. T for several elements showing significant deviation in the tendency to reach the Dulong and Petit values; b) C_p vs. T for several materials showing the impact of phase transitions on C_p , e.g. α -Mn (fcc) \rightarrow β -Mn (fcc) \rightarrow γ -Mn (fcc) \rightarrow δ -Mn(bcc).