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): $C_{p,m}(solid) = 3R = 24.9$ 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.

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

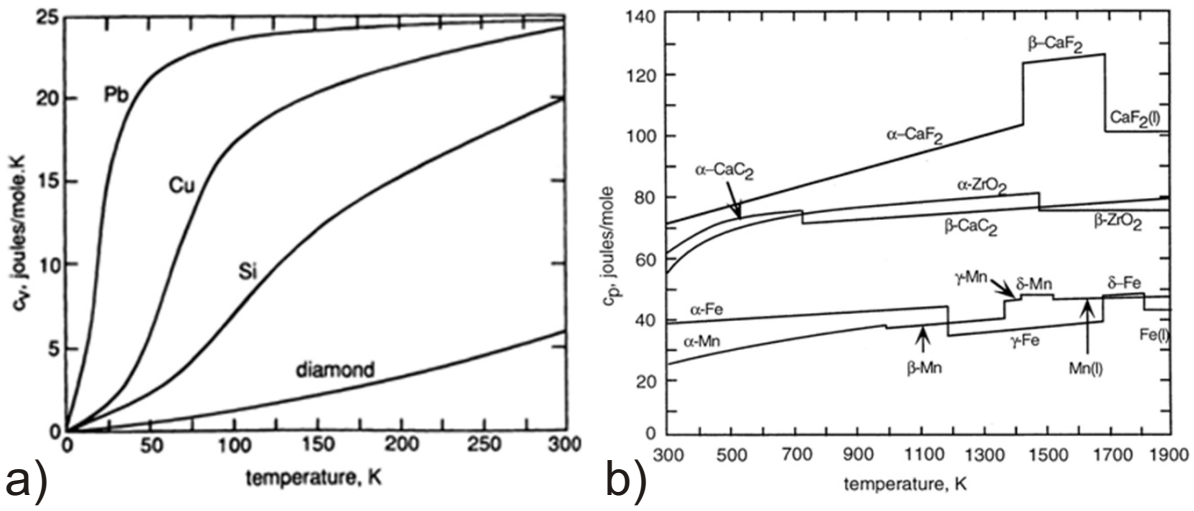

Figure 2.5: a) C_V vs. T for several elements showing significant deviation in the tendency to reach the Dulong and Petit values; b) C_p vs. T for several materials showing the impact of phase transitions on C_p, e.g. α-Mn (fcc) $\rightarrow$ β-Mn (fcc) $\rightarrow$ γ-Mn (fcc) $\rightarrow$ δ-Mn(bcc).