ENTROPY OF DIAMOND AND GRAPHITE

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In a quasistatic process, the relation between entropy, temperature and the heat flow is

$$dS = \frac{Q}{T} \tag{1}$$

where Q is the (infinitesimal) amount of heat flowing into or out of the system at temperature T. For a process at constant pressure but changing temperature, Q can be written in terms of the heat capacity C_P at constant pressure, since the amount of heat required to change the temperature by dT is $C_P dT$. In that case, the entropy change between temperatures T_i and T_f is

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P(T)}{T} dT \tag{2}$$

Example 1. From Schroeder's Figure 1.14, we can estimate a linear relation for C_P for a mole of diamond between $T = 300$ K and $T = 400$ K. Reading off the graph we get

$$C_P(300) = 6.5 \text{ J K}^{-1} \tag{3}$$

$$C_P(400) = 11 \text{ J K}^{-1} \tag{4}$$

Between these temperatures, a formula for $C_P(T)$ is therefore a straight line:

$$\frac{C_P(T) - 6.5}{T - 300} = \frac{11 - 6.5}{400 - 300} = 0.045 \tag{5}$$

$$C_P(T) = 0.045T - 7 \tag{6}$$

If we assume this is valid over the range of temperature from 298 K up to 500 K, we can get the entropy change over that range for a mole of diamond (incidentally, if you want to try this experiment, you'll need a very big diamond. A mole of diamond (carbon) is around 12 grams, and there are

5 carats per gram, so you're looking for a 60 carat diamond). The entropy change is

$$\Delta S = \int_{298}^{500} \frac{0.045T - 7}{T} dT \tag{7}$$

$$= [0.045T - 7\ln T]_{298}^{500} \tag{8}$$

$$= 5.47 \text{ J K}^{-1} \tag{9}$$

The entropy of a mole of diamond at $T = 298$ K is given in Schroeder's appendix as 2.38 J K^{-1} so the total entropy at $T = 500$ K is

$$S(500) = 2.38 + 5.47 = 7.85 \text{ J K}^{-1} \tag{10}$$

Example 2. An empirical formula obtained by fitting to measured data for C_P for one mole of graphite is

$$C_P = a + bT - \frac{c}{T^2} \tag{11}$$

where the constants are

$$a = 16.86 \text{ J K}^{-1} \tag{12}$$

$$b = 4.77 \times 10^{-3} \text{ J K}^{-2} \tag{13}$$

$$c = 8.54 \times 10^{5} \text{ J K} \tag{14}$$

The entropy change of a mole of graphite over the range of temperature from 298 K up to 500 K is therefore

$$\Delta S = \int_{298}^{500} \frac{a + bT - \frac{c}{T^2}}{T} dT \tag{15}$$

$$= \left[a\ln T + bT + \frac{c}{2T^2}\right]_{298}^{500} \tag{16}$$

$$= 6.59 \text{ J K}^{-1} \tag{17}$$

Adding on the tabulated value for $T = 298$ K we get

$$S(500) = 5.74 + 6.59 = 12.33 \text{ J K}^{-1} \tag{18}$$

The entropy of graphite is larger than that of diamond which we'd expect since diamond's crystal structure is more ordered than that of graphite.