

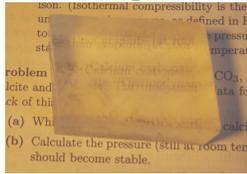
CALCITE AND ARAGONITE

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.28.

We can apply a similar analysis to that for graphite and diamond to calcium carbonate CaCO_3 , which also has two crystalline forms, calcite and aragonite. Calcite is a clear, colourless crystal which has the curious property of double refraction. Here's an image of a calcite crystal placed on Schroeder's problem 5.28:



You can see that a double image is produced.

Using the data in Schroeder's book, we can get some insight into the stability of these two forms by considering the Gibbs free energy. From the thermodynamic potential for the Gibbs free energy

$$dG = -S dT + V dP + \mu dN \quad (1)$$

we have

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad (2)$$

Ignoring compressibility, we can assume that V is constant as the pressure is increased. The molar volumes are $V_c = 36.93 \times 10^{-6} \text{ m}^3$ for calcite and $V_a = 34.15 \times 10^{-6} \text{ m}^3$ for aragonite. Therefore the Gibbs energies are

$$G_c = G_{c0} + 36.93 \times 10^{-6} P \quad (3)$$

$$G_a = G_{a0} + 34.15 \times 10^{-6} P \quad (4)$$

The constants of integration G_{c0} and G_{a0} can be found by requiring the energies to be those quoted in Schroeder for $P = 1 \text{ bar} = 10^5 \text{ Pa}$. The energies are $-1128.8 \times 10^3 \text{ J}$ for calcite and $-1127.8 \times 10^3 \text{ J}$ for aragonite. With these values, we have

$$G_{c0} = -1128.8 \times 10^3 - 3.693 \approx -1128.8 \times 10^3 \text{ J} \quad (5)$$

$$G_{a0} = -1127.8 \times 10^3 - 3.415 \approx -1127.8 \times 10^3 \text{ J} \quad (6)$$

So the energies are

$$G_c = -1128.8 \times 10^3 + 36.93 \times 10^{-6} P \quad (7)$$

$$G_a = -1127.8 \times 10^3 + 34.15 \times 10^{-6} P \quad (8)$$

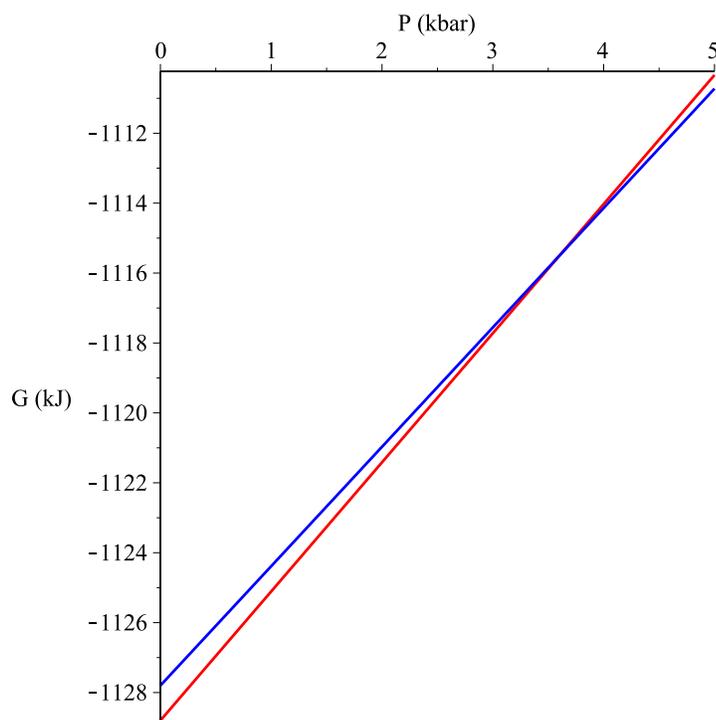
Since $G_c(P = 10^5) < G_a(P = 10^5)$, calcite is (very slightly) more stable than aragonite at atmospheric pressure and room temperature. To find the pressure at which aragonite becomes more stable, we set the two energies equal to each other:

$$-1128.8 \times 10^3 + 36.93 \times 10^{-6} P = -1127.8 \times 10^3 + 34.15 \times 10^{-6} P \quad (9)$$

$$P = 3.597 \times 10^8 \text{ Pa} \quad (10)$$

$$= 3.597 \text{ kbar} \quad (11)$$

Because the volumes are very similar, a plot of the two Gibbs energies shows two lines that are nearly parallel. In the plot, calcite is in red and aragonite is in blue.



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