

## Chapter 6 Answers

- Between 10 and 11°C, depending on how you do it. Actually there should also be some conductive cooling as well during a two kilometer rise of the fluid.
- If the reaction is written Graphite  $\rightarrow$  Diamond, then

$$\Delta_r G^\circ = 2900 \text{ J mol}^{-1}$$

$$\Delta_r V^\circ = -0.1881 \text{ J bar}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S^\circ = -3.363 \text{ J mol}^{-1} \text{ K}^{-1}$$

Letting  $P_2$  be the equilibrium pressure and  $P_1 = 1 \text{ bar}$ ,

$$\begin{aligned}\Delta_r G_{P_2}^\circ - \Delta_r G_{P_1}^\circ &= \Delta_r V^\circ (P_2 - P_1) \\ 0 - 2900 &= -0.1881 (P_2 - 1) \\ P_2 &= 1 + \frac{2900}{0.1881} \\ &= 15418 \text{ bars}\end{aligned}$$

To determine  $\Delta_r G^\circ$  at  $T_2 = 100^\circ\text{C}$ ,

$$\begin{aligned}\Delta_r G_{T_2}^\circ - \Delta_r G_{T_1}^\circ &= \Delta_r S^\circ (T_2 - T_1) \\ \Delta_r G_{T_2}^\circ - 2900 &= -(-3.363)(100 - 25) \\ \Delta_r G_{T_2}^\circ &= 3152.225 \text{ kJ mol}^{-1}\end{aligned}$$

so at  $100^\circ\text{C}$ ,

$$\begin{aligned}0 - 3152.225 &= -0.1881 (P_2 - 1) \\ P_2 &= 1 + \frac{3152.225}{0.1881} \\ &= 16759 \text{ bars}\end{aligned}$$

- Nepheline + Albite = 2 Jadeite

$$\Delta_r G^\circ = -14600 \text{ J mol}^{-1}$$

$$\Delta_r S^\circ = -64.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r V^\circ = 3.343 \text{ J bar}^{-1} \text{ mol}^{-1}$$

First get  $\Delta_r G^\circ$  at  $300^\circ\text{C}$ ,

$$\begin{aligned}\Delta_r G_{300}^\circ - \Delta_r G_{25}^\circ &= -\Delta_r S^\circ (300 - 25) \\ \Delta_r G_{300}^\circ &= 3192.5 \text{ J mol}^{-1}\end{aligned}$$

then find  $P_2$  for  $\Delta_r G_{P_2}^\circ = 0$ ,

$$\begin{aligned}\Delta_r G_{P_2}^\circ - \Delta_r G_{P_1}^\circ &= \Delta_r V^\circ (P_2 - P_1) \\ 0 - 3192.5 &= -3.343(P_2 - 1) \\ P_2 &= 956 \text{ bars}\end{aligned}$$

4. 158.5°C.
6. 1465°C.  $\alpha$ -quartz is metastable at this temperature. See Figure 17.8.
7. Using our data, the equations for the three boundaries are  
 Ky-And:  $P = 1 + 12.65(T - 154.65)$   
 And-Sill:  $P = 1 - 17.73(T - 602.85)$   
 Ky-Sill:  $P = 1 + 21.17(T - 259.96)$

These plot as in Figure 1. The lines meet at a point at 416.24°C, 3309.61 bars.

Using SUPCRT92 data and the same assumption of constant  $\Delta_r V$  and  $\Delta_r S$  gives a triple point at about 2980 bars, 433.5°C. However, using the univariant curve option in SUPCRT92 gives a triple point at 3816 bars, 501.5°C. The only difference between these two results is that the univariant curve option does not assume a constant  $\Delta_r S$ , but uses the Maier-Kelley heat capacity coefficients to evaluate this. It does assume a constant  $\Delta_r V$ . This is a good illustration of the error that can be introduced by the  $\Delta_r C_P^\circ = 0$  assumption.

Reactions involving only solid phases are extremely sensitive to small changes in the data, and the experiments on these phases are quite difficult for several reasons, so the exact location of this triple point is not very well known.

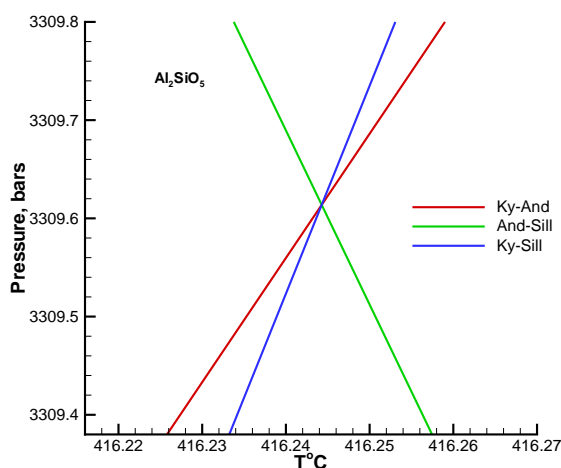


Figure 1:

8. (a)  $\alpha$  is more stable under standard conditions because it has a lower value of  $\Delta_f G^\circ$ .
- (b)  $\beta$  is the high- $T$  form because it has greater values of both  $\Delta_f H^\circ$  and  $S^\circ$ .
- (c)  $\beta$  is the high- $P$  form because it has a smaller  $V^\circ$ .
- (d) Recall that  $50 \text{ cm}^3 = 5.0 \text{ J bar}^{-1}$ , so

$$\begin{aligned}\frac{dP}{dT} &= \frac{\Delta_r S^\circ}{\Delta_r V^\circ} \\ &= \frac{S_\beta^\circ - S_\alpha^\circ}{V_\beta^\circ - V_\alpha^\circ} \\ &= \frac{93.4 - 90.0}{4.9 - 5.0} \\ &= \frac{3.4}{-0.1} \\ &= -34.0 \text{ bars/degree}\end{aligned}$$

(e)

$$\begin{aligned}\Delta_r G_P^\circ - \Delta_r G_{1 \text{ bar}}^\circ &= \Delta_r V^\circ (P - 1) \\ 0 - 3000 &= -0.1(P - 1) \\ P &= 30,001 \text{ bars}\end{aligned}$$

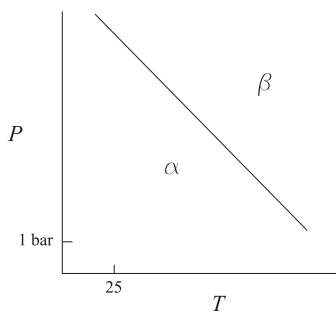


Figure 2: (f.)  $P$ - $T$  phase diagram of the  $\alpha$ - $\beta$  polymorphs.

- (h) The question is based on the example of silica solubility. Because no other data are given, you must assume that dissociation of  $\alpha$  into other dissolved species (ions) is not important. For the  $\alpha(s) = \alpha(aq)$  reaction,

$$\begin{aligned}\Delta_r G^\circ &= -2415 - (-2440) \\ &= 25 \text{ kJ} \\ &= -RT \ln K\end{aligned}$$

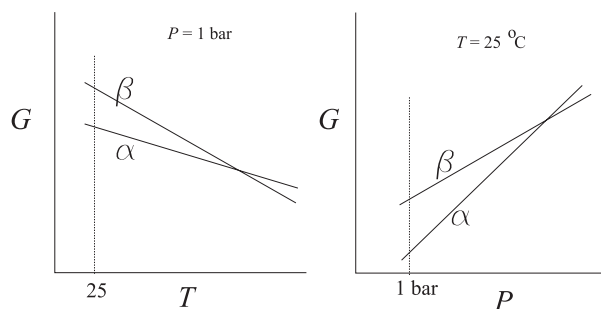


Figure 3: (g.)  $G$ - $T$  and  $G$ - $P$  sections through the phase diagram.

so

$$\begin{aligned}\log K &= \frac{-25000}{2.303 \times 8.3145 \times 298.15} \\ &= -4.380\end{aligned}$$

Assuming that  $a_{\alpha(s)} = 1$  and that  $a_{\alpha(aq)} = m_{\alpha}$ , the solubility of solid  $\alpha$  is  $10^{-4.38}$  molal.

- (i)  $\beta$  is a metastable form and will have a greater solubility. You can explain it by the effect of the larger  $\Delta_f G^{\circ}$  on  $\log K$ , or you can explain it to be the result of the fact that the metastable  $\rightarrow$  stable reaction is spontaneous, so it can take place by dissolution of the metastable form and precipitation of the stable form. The dissolution  $\rightarrow$  precipitation mechanism is one way to overcome the energy barrier which often prevents the spontaneous recrystallization of metastable phases.