

Chapter 17 Answers

1. $\Delta_f H_\beta^\circ = -18890 \text{ cal mol}^{-1}$.
2. $V_{\text{H}_2\text{O}(s)}^\circ = 19.688 \text{ cm}^3 \text{ mol}^{-1}$.
3. (a) Point 2 has four coexisting phases; maximum is three for one component. Point 2 may actually be two points close together. Point 5 has a triple point with one angle $> 180^\circ$, which is not possible. Each metastable extension must lie between two stable curves. You can prove this to yourself by drawing G - T or G - P sections.
 - (d) $V_E^\circ = 14.01 \text{ cm}^3 \text{ mol}^{-1}$.
 - (e) $S_C^\circ = 21.26 \text{ J mol}^{-1}$.
 - (f) $P_7 = 501.7 \text{ bar}$.
 - (g) $15.0 > V_B^\circ > 11.62 \text{ cm}^3 \text{ mol}^{-1}$.
 - (h) Point 6 is a critical point. E is liquid. F is vapor or gas. Others are solids. Solid A floats. Solids B, C, D, G sink.
 - (i) The slope dP/dT is not constant because $\Delta S/\Delta V$ is not constant, and this, in turn, is because the properties of phase F (a gas) change more rapidly with P , and to a lesser extent T , than do the properties of solids and liquids.
4. PERFECT EQUILIBRIUM COOLING HISTORY OF COMPOSITION 6.
 - Homogeneous liquid of composition 75% B, 25% A cools to top of miscibility gap, and a second liquid (L_1 , composition 86% B, 14% A) separates. On cooling, compositions of original liquid (now called L_2) and L_1 follow sides of miscibility gap. Given enough time, these two liquids would probably split into separate layers, like oil and water.
 - At T_1 , L_1 is 91% B, 9% A; L_2 is 68% B, 32% A. Proportions are about 70% L_2 and 30% L_1 .
 - On further cooling, liquid compositions follow miscibility gap to the eutectic temperature between T_1 and T_2 .
 - At the eutectic T , crystals of pure B and liquid L_2 form from liquid L_1 . The reaction can be written $L_1 \rightarrow L_2 + B$. During this reaction, the phase proportions change from 31% L_1 , 69% L_2 to 23% crystals of B, 77% liquid L_2 . The temperature stays constant until liquid L_1 is used up.
 - When the last drop of L_1 disappears, cooling resumes. Crystals of B form as the liquid becomes richer in A, following the liquidus. As there are no longer two liquids, we refer simply to the liquid, rather than to L_2 .
 - At T_2 liquid composition is 60% B, 40% A. Proportions are about 38% crystals of B, 62% liquid.
 - At T_3 , liquid composition is 55% B, 45% A. Proportions are about 44% crystals of B, 56% liquid.

- Cooling continues to the eutectic below T_3 , where the liquid has composition 53% B, 47% A. At the eutectic, crystals of solid solution α_2 (composition 48% B) and crystals of B form simultaneously while the temperature remains constant until the liquid is all gone ($L \rightarrow \alpha_2 + B$). During this reaction, the phase proportions change from 53% liquid, 47% crystals of B to about 48% crystals of α_2 , 52% crystals of B.
- When the last drop of liquid disappears, cooling of the now completely solid mass of crystals continues. The crystals of α_2 become steadily richer in A while remaining completely homogeneous. This requires that component B diffuse out of the crystals of α_2 and form crystals of B.
- At T_4 , α_2 composition is 43% B, 57% A. Proportions are about 56% crystals of B, 44% crystals of α_2 .
- Cooling continues to the eutectoid below T_4 , where α_2 has composition 42% B, 58% A. At this temperature, crystals of solid solution β_2 (41% B, 59% A) and crystals of B form simultaneously ($\alpha_2 \rightarrow \beta_2 + B$). During this reaction, the phase proportions change from 57% crystals of B, 43% solid α_2 , to 58% crystals of B, 42% solid β_2 . (The terms *peritectoid* and *eutectoid* refer to the same geometrical relationships on diagrams as peritectic and eutectic, except that all phases are solids.)
- When the last crystal of α_2 disappears, cooling of the crystals of β_2 and B continues, while β_2 exsolves B and becomes steadily richer in A.

PERFECT FRACTIONAL COOLING HISTORY OF COMPOSITION 2.

We will discuss fractional crystallization in terms of zoned crystals. As mentioned in §11.4.8, the same result can be obtained by physically separating the newly-formed crystals from the liquid.

- Starting homogeneous liquid composition is 80% A, 20% B. At T_A , first crystals of solid solution α_1 appear, composition 98% A, 2% B. On cooling, liquid composition follows the liquidus, while the *surface* of existing crystals and any new crystals of α_1 have compositions given by the solidus. No homogenization within the crystals takes place, so that crystals are *zoned*, with centers richer in A than the margins. The liquid is always completely homogeneous. Alternatively, we could say that crystals are separated from the liquid as soon as they form. The effect of separation or zoning is that once a crystal forms, it does not later react with the liquid.
- On continued cooling, the surface composition of crystals follows the solidus, liquid composition follows the liquidus.
- At T_B a peritectic is reached. Liquid (composition 35% B, 65% A) coexists with crystals of α_1 , which are zoned in composition, the outermost layer of all crystals being 10% B, 90% A. These react with the liquid to form a layer of solid solution β_1 (composition 12% B, 88% A) on the surface of all crystals, so that the liquid now “sees” only crystals of β_1 . No plateau on the cooling curve is observed, that is, *there is no 3-phase equilibrium*. (In equilibrium cooling, the reaction at T_B would be $L + \alpha_1 \rightarrow \beta_1$.)

- Cooling continues. Layers of solid solution β_1 of composition shown by the solidus continue to coat the crystals, while the liquid gets richer in B.
- Cooling continues to T_C (another peritectic). Liquid (39% B) coexists with zoned crystals, some of which have centers of composition 2% B (only “some,” because some crystals nucleate during the cooling history and therefore would have center compositions somewhere between 2% B and 13% B). The surfaces of all crystals are β_1 with composition 13% B, 87% A. At T_C a layer of solid solution α_2 is deposited on all crystals. The liquid is *not* used up (as it would be in equilibrium cooling), and no plateau on the cooling curve is observed. (In equilibrium cooling the reaction at T_C would be $L + \beta_1 \rightarrow \alpha_2$.)
- Cooling continues. Layers of solid solution α_2 of composition shown by the solidus continue to coat the crystals, while the liquid follows the liquidus, getting richer in B.
- At T_D (eutectic), liquid reaches the eutectic composition 53% B, 47% A, which coexists with zoned crystals, some of which contain β_1 and α_1 all the way back to 2% B. The surfaces of all crystals are α_2 with composition 48% B, 52% A. Crystals of B and α_2 (48% B) crystallize simultaneously until the liquid disappears ($L \rightarrow \alpha_2 + B$). The temperature remains constant during the coexistence of these three phases. The crystals produced during crystallization at the eutectic temperature are not zoned (there is no difference in crystallization at a eutectic in fractional and equilibrium processes). The proportions of phases produced during crystallization at T_D are 90% α_2 , 10% crystals of B. When the last drop of liquid disappears, the *average* composition of all solid phases (the composition you would get if you ground up all the solids together and analyzed the mixture) is the same as the bulk composition (composition 2). Therefore, a (curved) line showing the average solid composition would start at T_A , 2% B, and end at T_D , 20% B.
- After disappearance of the liquid, cooling of the crystals of B and the zoned crystals continues with no further changes in composition. This is because the crystals can only change composition (stay on the solvus lines) if components A and B can diffuse through the crystal structures. However, this has been ruled out in the case of perfect fractional crystallization. If it was possible, the zoned crystals would have homogenized.
- Note that in fractional crystallization, some crystals of pure B appear, whereas in equilibrium crystallization no phase having more than 39% B would ever appear. This illustrates the importance of fractional crystallization in natural processes, that is, a crystallizing liquid can generate phases of much greater compositional variation during fractional crystallization than during equilibrium crystallization.

Note: These cooling histories are called “Perfect” Fractional Crystallization and “Perfect” Equilibrium Crystallization because they are the two hypothetical extremes of a complete spectrum of possible (or imperfect) cooling histories. In

possible or realistic cooling histories, complete equilibrium is not attained, but neither are crystals separated from the melt immediately on forming, and some solid-state diffusion and crystal homogenization takes place.

A Mass Balance

Consider composition 2 at T_1 , at equilibrium (no fractional crystallization). We have

Phase	Composition	Proportion
solid α_1	4% B, 96% A	32%
liquid	28% B, 72% A	68%

Mass balance on component B:

$$(0.04 \times 32) + (0.28 \times 68) = 20.32$$

which is approximately the percentage of B in the bulk composition. Try the same thing for component A. The two answers, each slightly inexact because you cannot read the diagram with perfect accuracy, should add to exactly 100%.

5. (b) Eutectic at approximately 38°C, 35% B.
(d) Liquid proportion: $(35/45) \times 1.5 \text{ g} = 1.17 \text{ g}$.

Solid proportion: $(10/45) \times 1.5 \text{ g} = 0.33 \text{ g}$.

6. (c) $T_m A = 60^\circ\text{C}$. $T_m B = 880^\circ\text{C}$. Two polymorphs, transition T 275°C. $S_\beta^\circ = 6.0 \text{ J mol}^{-1} \text{ K}^{-1}$.
7. Any way of looking at it that obeys the Phase Rule is right. Choose the one that suits you. The phase transition loop becomes detached from the temperature axis for component A when solution 1 is liquid, solution 2 is vapor, and the pressure of the $T-X$ section is above the critical pressure of A, and similarly for B. Therefore, the loop may become detached from one or both axes.
8. There are reasons why ice-IX does not exist, but they are not within equilibrium or “classical” thermodynamics, the subject of this book. Thermodynamics does not so much “explain” energetic relationships as define parameters and methods of measurement and calculation that bring order to our knowledge of existing substances. To understand why this order exists, and not some other kind of order, you must go to statistical and quantum chemistry. If ice-IX did exist, its melting temperature would have to be $> 0^\circ\text{C}$ or 32°F , and 114.4°F is as good a number as any.
9. (a) See Figure 1.
(b) Ice V sinks in water.
(c) See Figure 2.

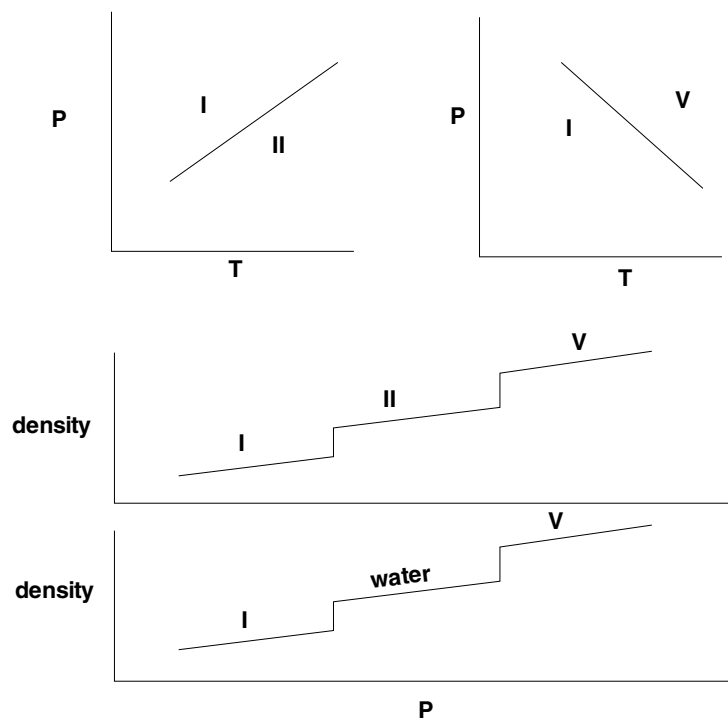


Figure 1:

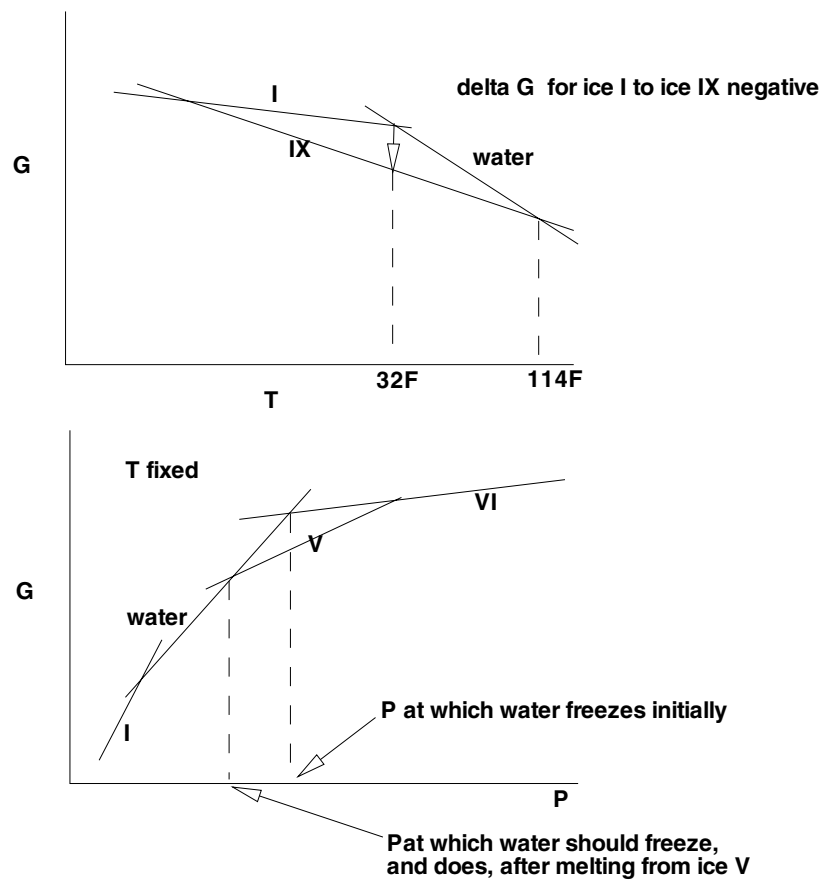


Figure 2: