Chapter 17 Problems

1. If the slope of a phase transition of a mineral from phase α to phase β is -21.0 bar deg^{-1} at a temperature of 600 K, the $\Delta_{\alpha\rightarrow\beta}V$ of the transition is $+0.150$ cal bar^{-1}, and $\Delta_f H^\circ_{600}$ of phase α is $-17,000$ cal mol^{-1}, what is $\Delta_f H^\circ_{600}$ of phase β? Sketch and label the phase diagram.

2. The slope of the ice–water phase boundary is -131.7 bar deg^{-1}. Knowing the heat of fusion of ice ($\Delta_{ice\rightarrow water}H^\circ = 6010$ J mol^{-1}) and the molar volume of water at 0°C ($V^\circ_{\mathrm{H_2O}(l)} = 18.01826$ cm^3 mol^{-1}), calculate the molar volume of ice at 0°C.

3. A hypothetical compound β has been found to have at least 7 phases, named A, B…G, arranged as shown in Figure 1. Point 6 is a critical point. The locations of points 1, 2…7 and some of the thermodynamic properties have been found experimentally to have the following values:

Point	T°C	P bar
1	277	132
2	236	256
3	270	404
6	483	179
7	157	

Phase	V°, cm^3 mol^{-1}	S°, J mol^{-1} K^{-1}
A	15.0	22.0
C	11.62	
D	10.0	21.4
E		22.3

   (a) There are two parts of this diagram that are thermodynamically impossible. Where are they, and why are they incorrect? Sketch possible correct relationships at each location.

   (b) Sketch G–P and V–P sections at 250°C.

   (c) Sketch G–T and H–T sections at 150 bar.

   (d) Calculate V°_{E}.

   (e) Using this result, calculate S°_{C}.

   (f) Calculate the pressure at point 7. If it doesn't look about right compared to the diagram, you have made a mistake.

   (g) What are the upper and lower limits for possible values for V°_{B}?

   (h) Identify each phase as solid, liquid, or gas. Which solids float and which sink in liquid β?

   (i) Why are boundaries A–F and E–F curved, while all the others are straight?

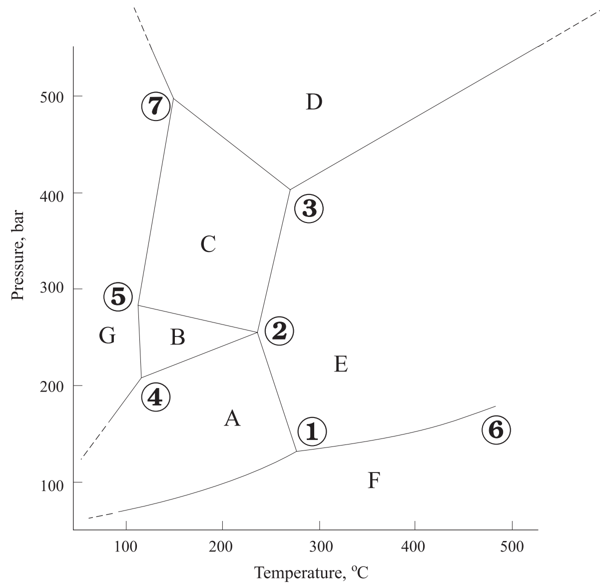

Figure 1: Phase diagram for compound β.

4. (a) Describe in detail the equilibrium cooling history of a liquid of composition 6 in Figure 2.

   (b) Describe in detail the perfect fractional cooling history of a liquid of composition 2 in Figure 2.

   This diagram looks frighteningly complex at first, but it contains nothing more than the diagram elements already discussed, and working through such a diagram is not more difficult than a simpler diagram; it just takes longer.

5. You have performed a series of experiments in the lab involving the cooling of various mixtures of compound A and compound B at 1 atm. The results of the experiments are given in the table below, in which T represents the temperature at which you first observed crystals in the cooling mixtures.

Run no.	Composition (wt.%)	T°C
1	100% compound A	63
2	100% compound B	88.9
3	90% "	85.4
4	75% "	75
5	60% "	63.9
6	45% "	50.5
7	30% "	42.9
8	15% "	54.4

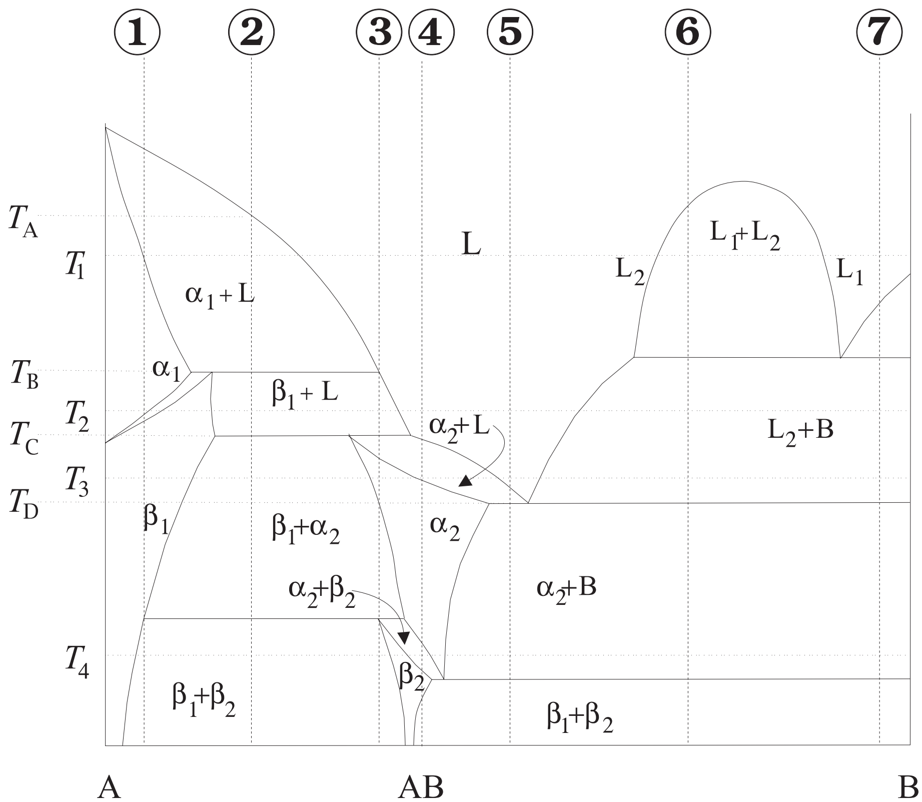

Figure 2: $T\!-\!X$ phase diagram for the system A–B.

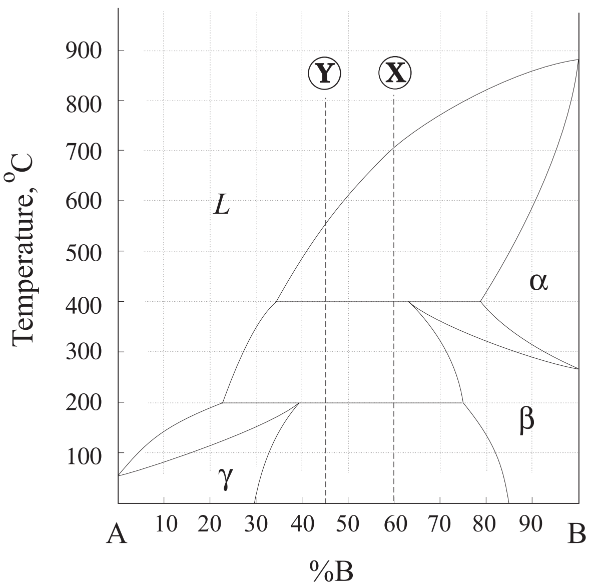

Figure 3: System A–B at 1 bar pressure.

(a) Construct a phase diagram using as axes T°C and wt.% B and label all the phase fields. Assume no appreciable solid solution in the solid phases.

(b) What are the eutectic temperature and composition?

(c) Construct a schematic cooling curve (temperature vs. time) for run no. 4.

(d) Consider 1.5 g of a system containing 35 wt.% compound A and 65 wt.% compound B at a temperature of 60°C. What phases are present at equilibrium, and how much of each phase is there? (Note that this information is contained in the diagram, even though no such experiment has been conducted.)

6. (a) Describe the equilibrium cooling history of a liquid of composition Y in Figure 3. Give the compositions and proportions of the phases before and after the phase transitions. Calculate at least one mass balance.

(b) Describe the fractional crystallization of a liquid of composition X in Figure 3.

(c) What are the melting points of pure A and pure B? How many polymorphs of component B are there? What is the temperature of transition between them? If the entropy of α is $10\,\mathrm{J\,mol^{-1}\,K^{-1}}$, what is the entropy of β? $\Delta_f G^\circ_\alpha = -100\,\mathrm{kJ\,mol^{-1}}$, $\Delta_f G^\circ_\beta = -101\,\mathrm{kJ\,mol^{-1}}$.

(d) Figure 3 could be described as being made up of a simple melting loop intersected by a miscibility gap, complicated slightly by the polymorphs of component B. If component B had only one crystal form (α), what would the phase diagram look like?

(e) If liquid immiscibility developed at higher pressures, what might the diagram look like: (a) B having only one crystal form; (b) B having two polymorphs?

7. In the text it says that there are two basic binary diagram elements. However, note that if the phase transition loop (Figure 17.21, left) becomes detached from the vertical axes on both sides, and if the solvus (Figure 17.21, right) closes downward as well as upwards (i.e., has both upper and lower consolute points; this happens in some systems), the two elements become indistinguishable. So perhaps there is only one "basic element." Then again, these elements are created by tie-lines, so perhaps the "basic elements" are the two-phase and three-phase tie-lines. Which point of view is right? Under what circumstances does the phase transition loop become detached from the temperature axes?

8. A central part of the novel *Cat's Cradle* by Kurt Vonnegut, Jr., involves the existence of a new polymorphic form of ice (ice-IX), which is more stable than ordinary ice (ice-I) at atmospheric pressure and has a melting point of 114.4°F (45.8°C). When ice-IX gets loose it acts as a seed, and all the water on Earth, which is metastable with respect to ice-IX, freezes immediately. This, of course, means the end of life on Earth. Is there any thermodynamic reason why ice-IX could not exist? If it did exist, is 114.4°F a reasonable melting point for it? Answer this with the help of a G–T section through system H_2O at 1 bar.

9. Construct the phase diagram for H_2O in the range 0 to 7000 bar (Y-axis), -40°C to 20°C (X-axis), using the data tabulated below. Label each phase boundary and triple point with the coexisting phases and degrees of freedom. Show the metastable extensions of the phase boundaries.

Point	Phases	T°C	P bar
a	ice-I, ice-III, L	-22	2215
b	ice-III, ice-V, L	-17	3530
c	ice-I, ice-II, ice-III	-35	2170
d	ice-II, ice-III, ice-V	-24	3510
e	ice-V, ice-VI, L	0.2	6380
f	ice-VI, ice-VII, L	81.6	22400
	(point f is off the diagram).		

(a) The slope of the ice-II—ice-V boundary is negative, and the slope of the ice-I—ice-II boundary is positive (you don't need to know the exact slopes). Sketch a diagram of density vs. pressure (0 to 5000 bar) for H_2O at -40°C and at -10°C, with no numbers on the density axis.

(b) Does ice-V sink or float in water?

(c) Sketch a G–P section through the diagram at -10°C from 0 to 7000 bar showing ice-I, water, ice-V, and ice-VI. Show the location on this section of the freezing of water to ice-VI and ice-V as discussed in the quotation from Bridgman (quotation in text). Why does water freeze sometimes to ice-V and sometimes to ice-VI, according to Bridgman?