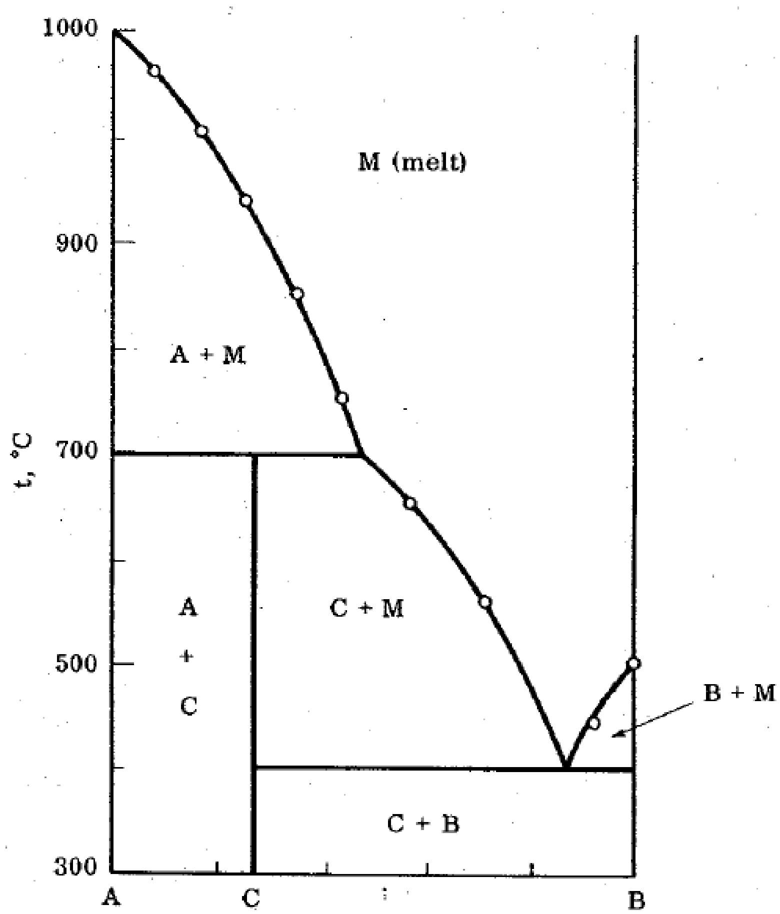
Solutions to Problem Set 10

Ref.: A. W. Adamson, Understanding Physical Chemistry (W. A. Benjamin, Inc. 1969)

A. Constructing phase diagrams from cooling curves

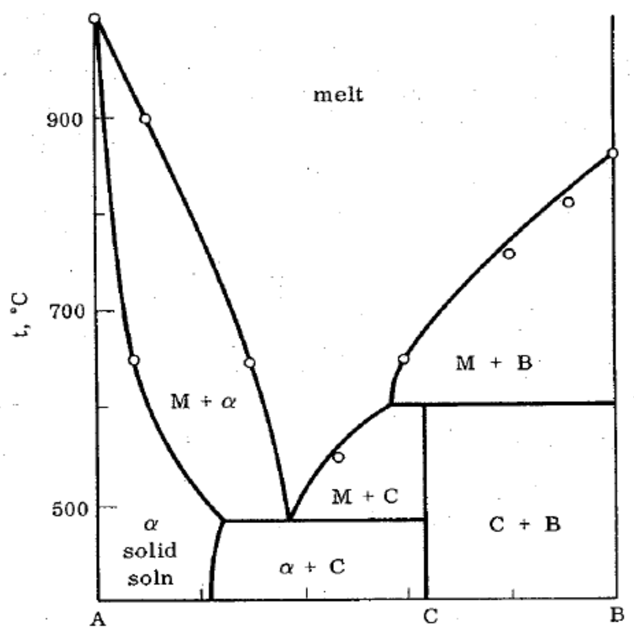
1.



Each halt corresponds to a line of three-phase equilibrium and each break corresponds to a boundary between a one-phase and a two-phase region. The simplest diagram is that shown to the left.

An unstable compound is indicated that must contain less than 80% A and more than 70% A, since it is between these limits that the lower three-phase line appears. A good guess is 75% A, corresponding to a compound of formula A_3B.

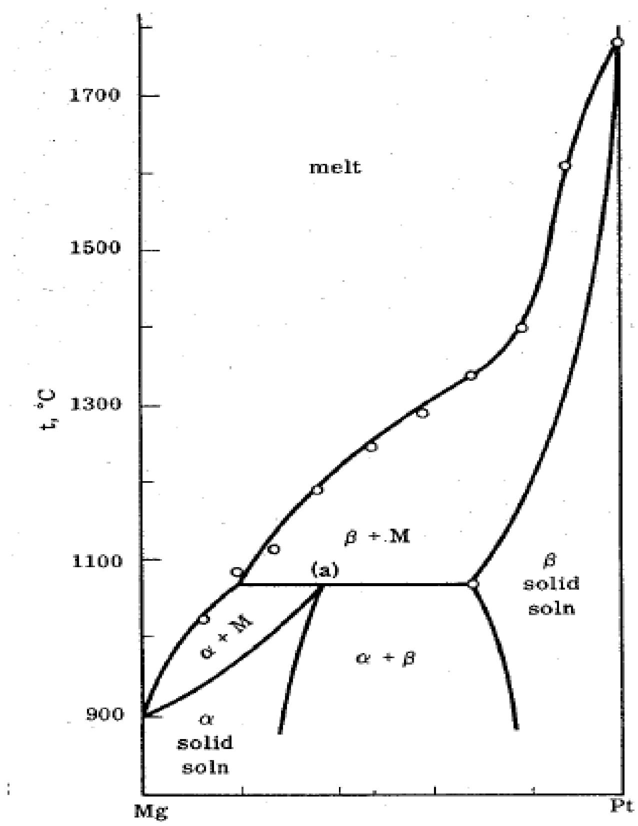
2.



The break and halt data are used to plot the points in the diagram to the left.

The simplest explanation for the two halts at 60%B is that an unstable compound forms. Its composition must lie between 60% B and 80% B, and if it is 75% B, the formula would be AB_3. Alternatively, it might be AB_2 (as 67%B is between 60% and 80% B).

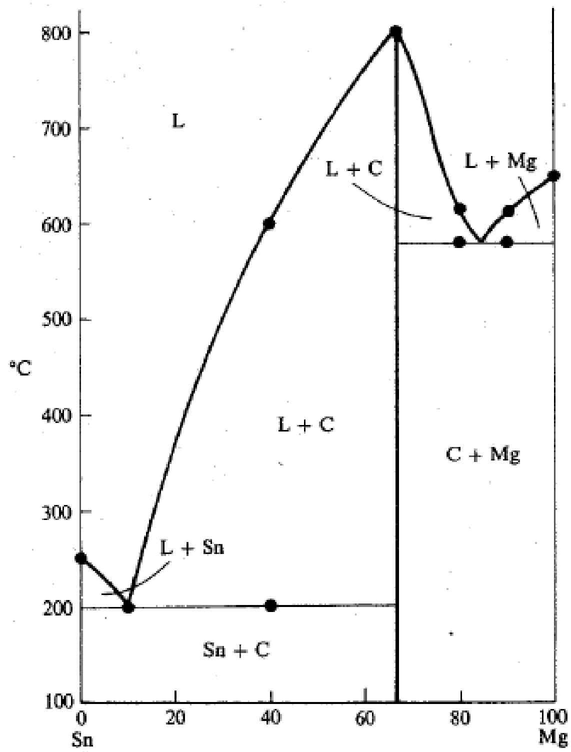
3.



A halt temperature lying between the melting points of the pure components suggests a peritectic type diagram, as seen on the left, where the break and halt points from the given cooling curves have been plotted.

The phase reaction is:
phase + melt → α phase
For compositions with more Mg than point (a) in the diagram above, upon cooling, the β phase disappears before melt does. On the other hand, for compositions with more Pt than point (a) in the diagram above, upon cooling, melt disappears before the β phase does.

4.



We note in the data, the presence of a congruent melting point at 67% Mg, thus we identify a compound with this composition with the chemical formula Mg_2Sn. Thus, plotting the given break and halt points (on the left diagram) provides an easy interpretation..

5.

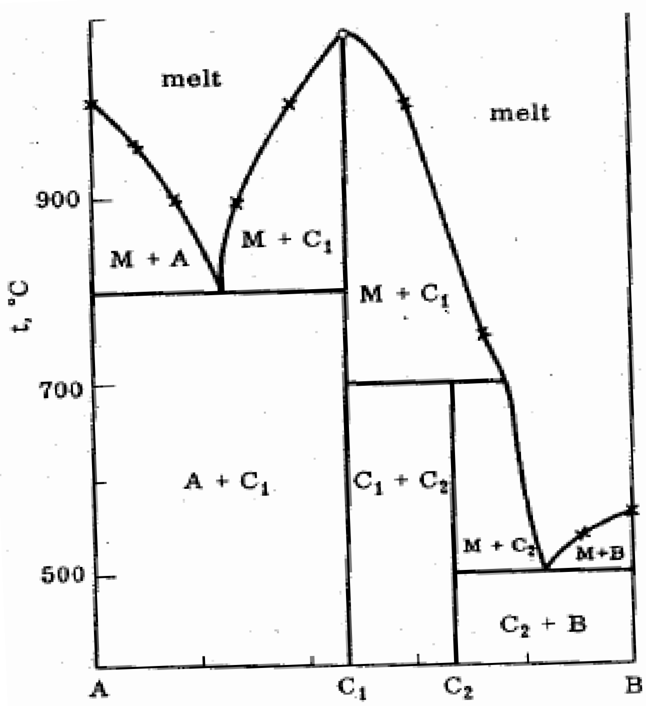
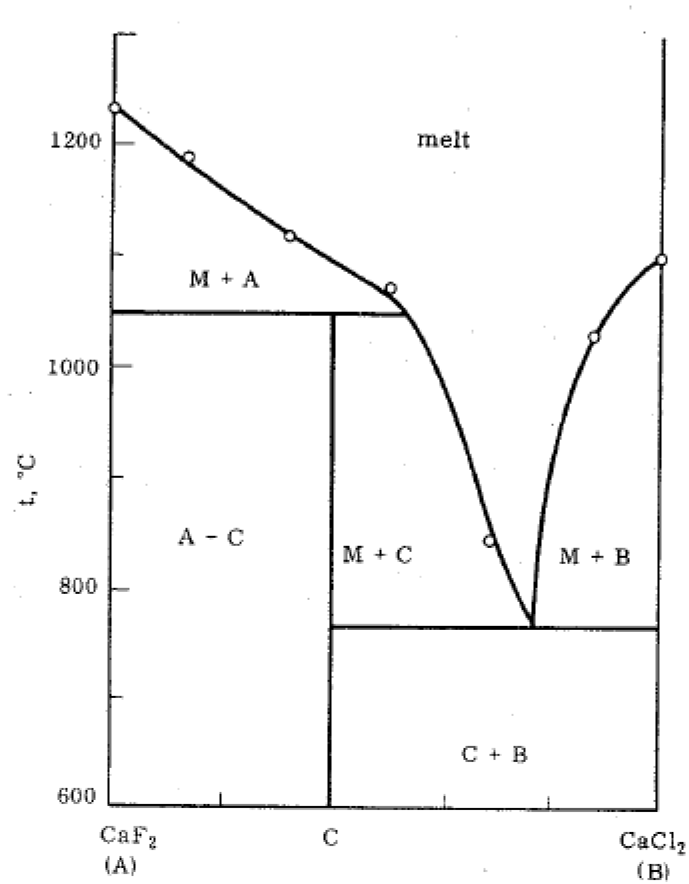


FIGURE 12-36

From the given data, the halt at 1100°C with no break, a congruently melting compound C_1 is evident at 50%, with corresponding formula AB. The double halt for the 30% melt suggests an unstable compound. Its composition must lie between 40% A and 36% A; if 33.3% then the formula of the compound C_2 would be AB_2.

6.

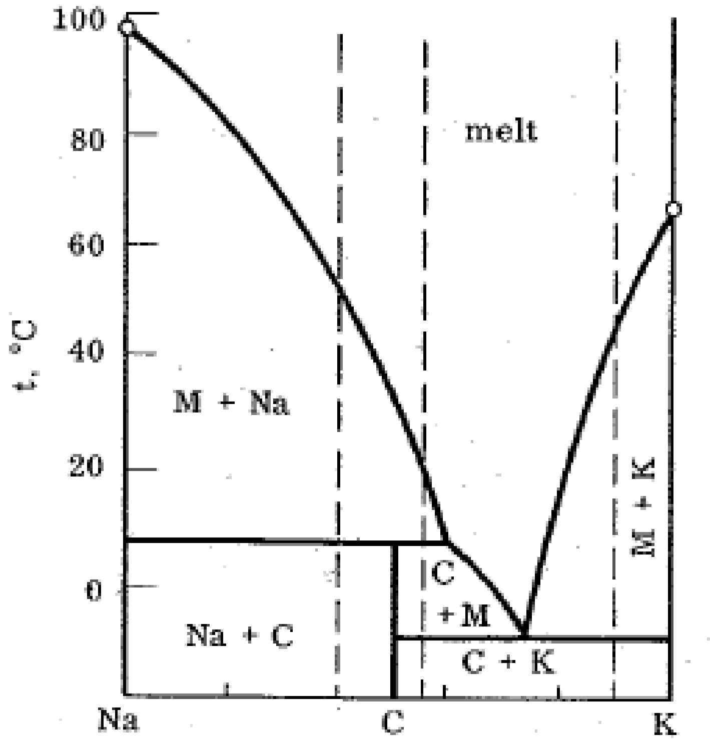


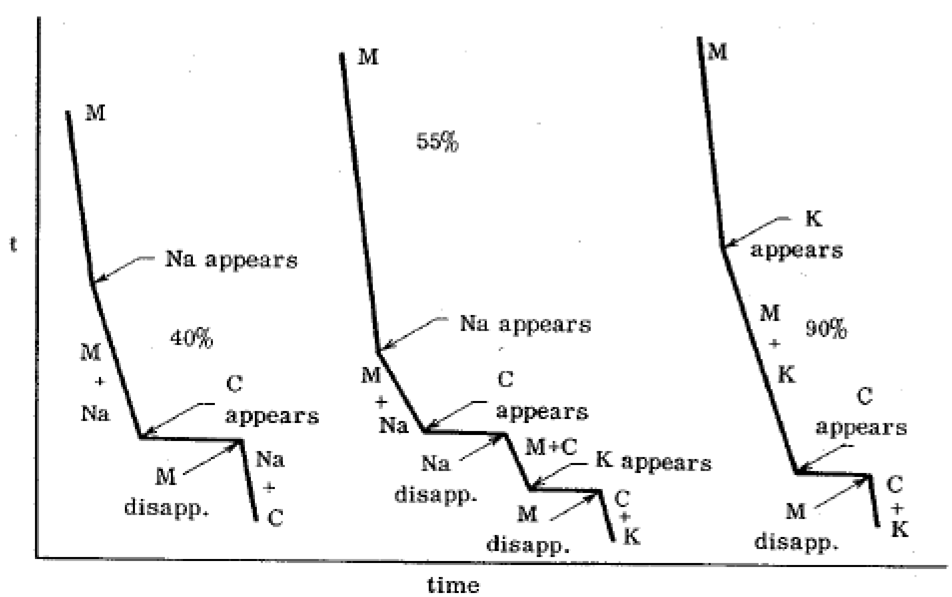
The cooling curves at 0% and 100% $CaCl_2$ obviously give the melting points of the pure components. The two halts shown in the cooling curve at 50% suggest unstable compound formation, if the compound has a composition lying between 30% and 50% $CaCl_2$. We choose it as probably 40% $CaCl_2$, which corresponds to the formula A_3B_2 or $(CaF_2)_3(CaCl_2)_2$.

B. More on Compound formation

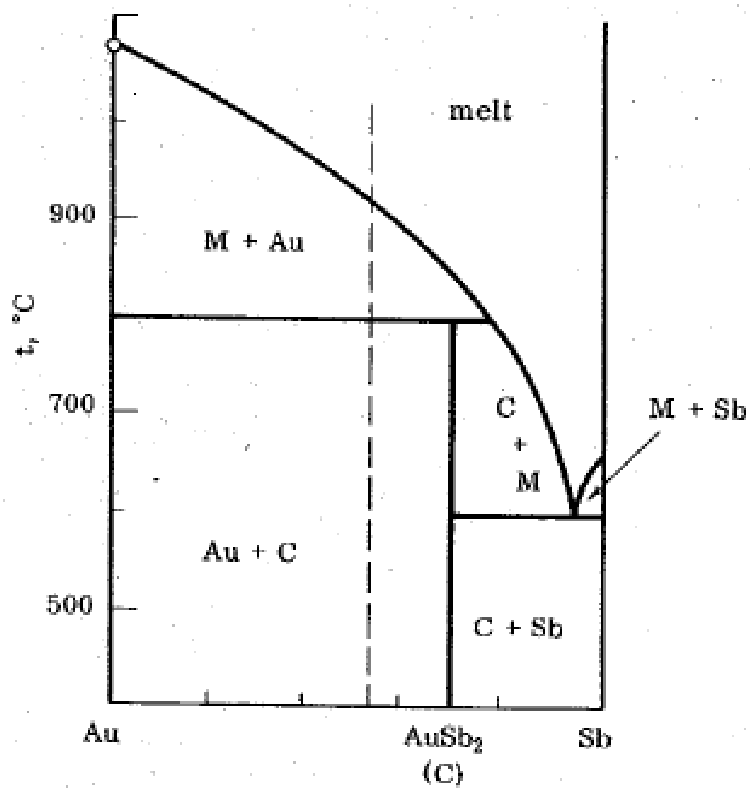
7.

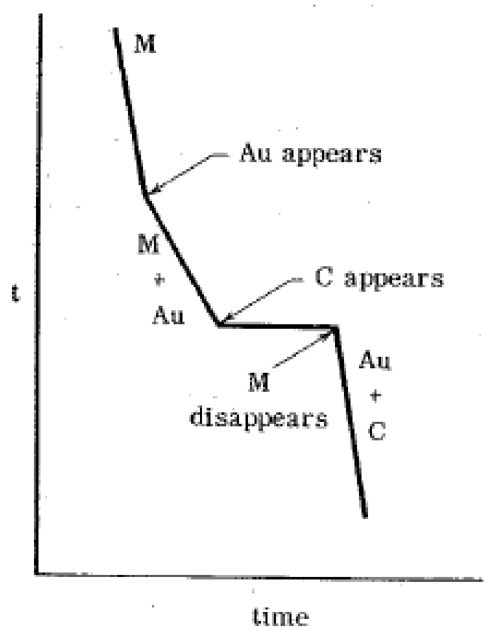
Since the compound decomposes into a melt richer in K than the compound, then the residual solid must therefore be richer in Na. The simplest assumption is that the residual solid is pure Na.



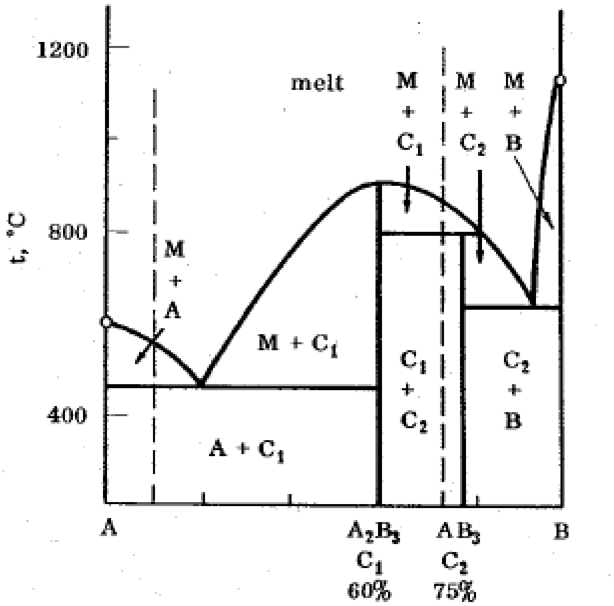


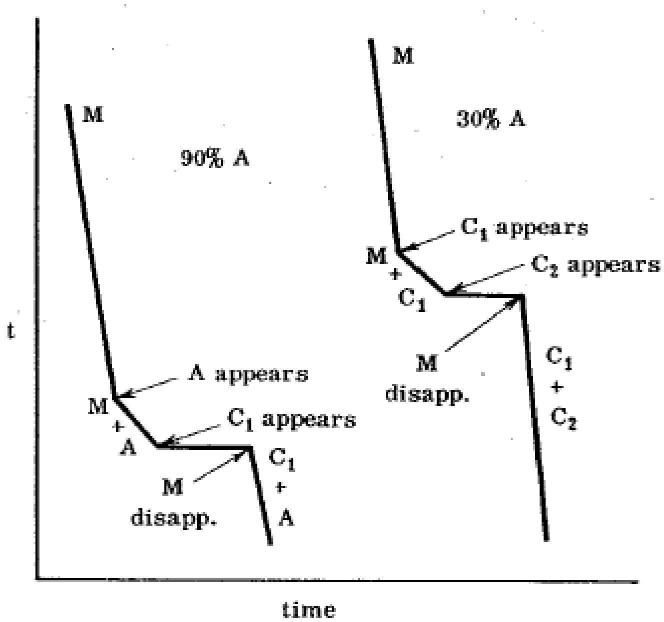
8. Since the incongruently melting compound decomposes above the melting point of Sb but below the melting point of Au, the simplest assumption is that solid pure Au is one of the decomposition products, and a melt, of > 67% Sb is the other. The additional eutectic provides a simple way to connect up the known data.





9. The composition of the first eutectic melt could lie either to the right or to the left of the 90% B composition point. Here we choose to the right.

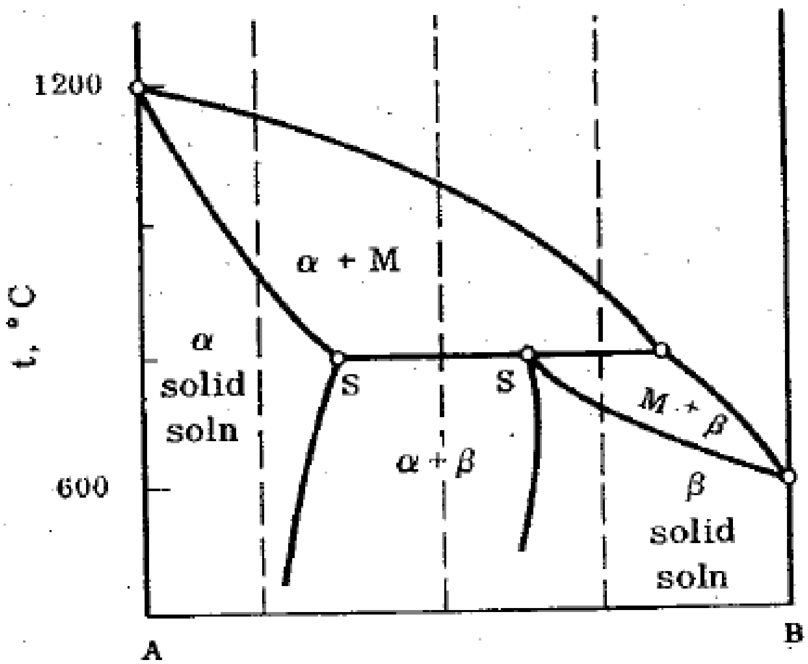


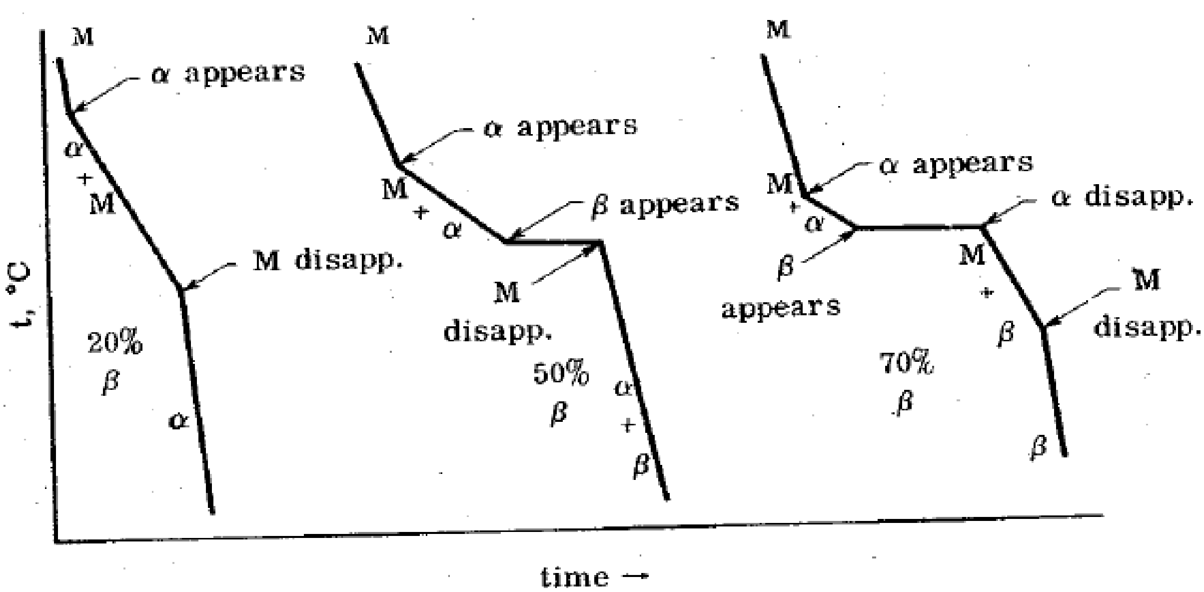


If, on the other hand, it lay to the left, then the order of appearance of A and C would be the reverse of that shown in the cooling curve above.

C. More on Peritectic systems

10. The coexistence of three phases, two solid at a temperature between the two melting points is a clear indication of a peritectic type diagram.





11. Labels are indicated below