

8.10: Cooling Curves

The method that is used to map the phase boundaries on a phase diagram is to measure the rate of cooling for a sample of known composition. The rate of cooling will change as the sample (or some portion of it) begins to undergo a phase change. These “breaks” will appear as changes in slope in the temperature-time curve. Consider a binary mixture for which the phase diagram is as shown in Figure 8.10.1A. A cooling curve for a sample that begins at the temperature and composition given by point a is shown in Figure 8.10.1B.

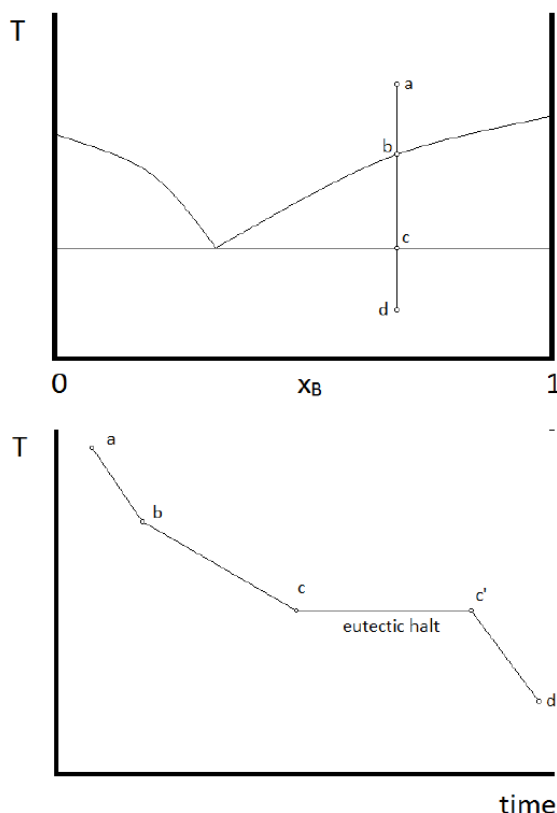


Figure 8.10.1: (A) cooling of a two-component system from liquid to solid. (B) Corresponding cooling curve for this process.

As the sample cools from point a, the temperature will decrease at a rate determined by the sample composition, and the geometry of the experiment (for example, one expects more rapid cooling if the sample has more surface area exposed to the cooler surroundings) and the temperature difference between the sample and the surroundings.

When the temperature reaches that at point b, some solid compound B will begin to form. This will lead to a slowing of the cooling due to the exothermic nature of solid formation. But also, the composition of the liquid will change, becoming richer in compound A as B is removed from the liquid phase in the form of a solid. This will continue until the liquid attains the composition at the eutectic point (point c in the diagram.)

When the temperature reaches that at point c, both compounds A and B will solidify, and the composition of the liquid phase will remain constant. As such, the temperature will stop changing, creating what is called the **eutectic halt**. Once all of the material has solidified (at the time indicated by point c'), the cooling will continue at a rate determined by the heat capacities of the two solids A and B, the composition, and (of course) the geometry of the experimental set up. By measuring cooling curves for samples of varying composition, one can map the entire phase diagram.

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