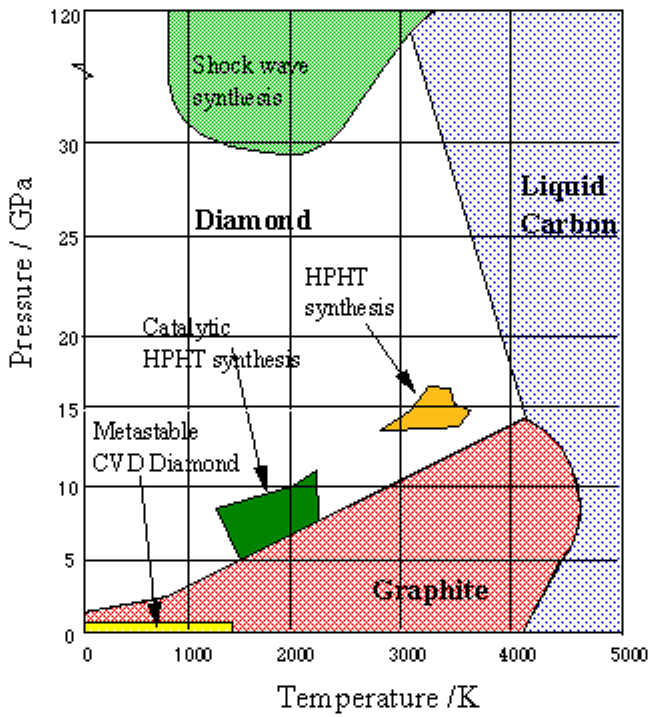
Phase diagram of carbon



Lecture 10

Simple eutectic systems

Greek, Eutektos – easily melting
Eu – good, well + tekein – to melt

Motivation:

A two component system is the simplest of multicomponent systems.

A condensed phase rule is the one used to represent the phase diagram of a condensed system, either liquid or solid. In such a case, for two or more components, the phase diagram becomes multidimensional.

Look at, $F = C - P + 2$, for one phase, $2 - 1 + 2 = 3$ and the phase diagram will have three dimensions. This is difficult to represent. For larger number of components, the situation becomes complicated.

Simplification:

One way to reduce complexity is to disregard the vapour phase in all discussions. In fact the error involved in this is not large.

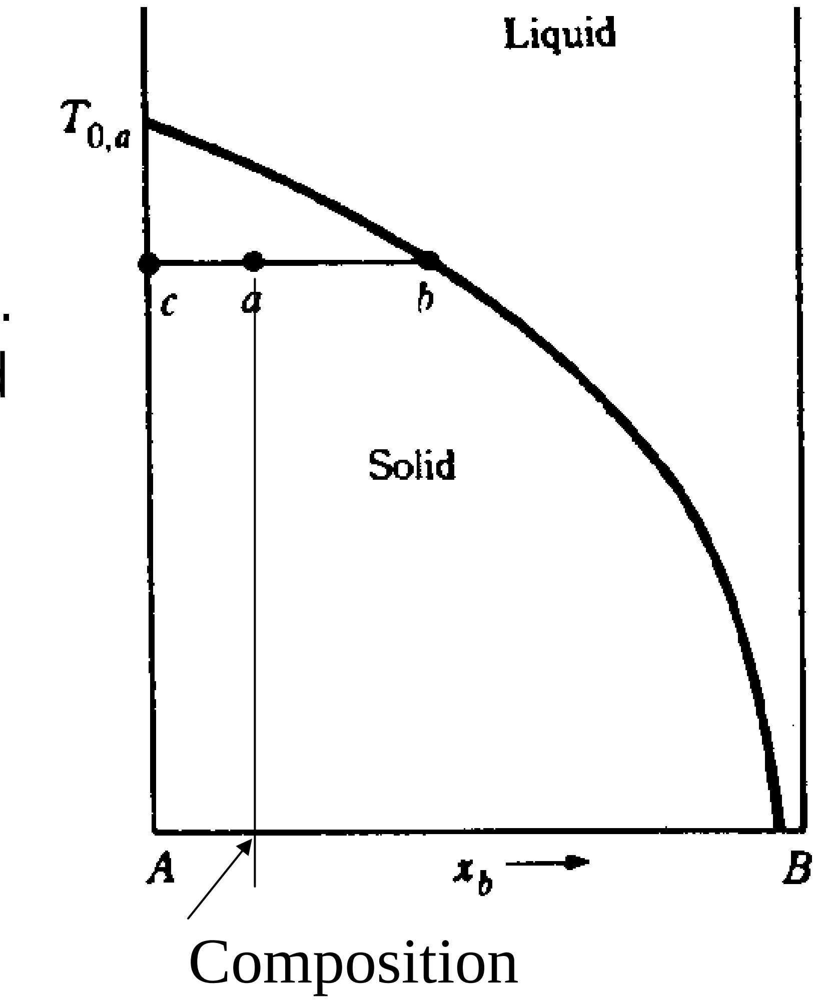
Another way is to fix one of the variables, say pressure and discuss the phase diagram at constant pressure. This option is satisfactory as most of the phase changes of importance occur at atmospheric pressure. This phase rule, which is the condensed phase rule can be represented as $F' = C - P + 1$, when pressure is constant.

When a mixture of A and B is cooled, solid will separate at a the freezing point which will vary with composition. This variation can be represented by the equation,

$$\ln x_A = - \Delta H_{fus,A}/R\ (1/T - 1/T_{0A}),$$

Where x refers to the mole fraction and rest of the quantities have their usual meaning. T_{0A} is the pure A melting point.

This variation is depicted.
The region above the line is the liquid and below is solid.
The curve is called the liquidus curve.
At a point represented by a, the liquid of composition b is in equilibrium with solid A of composition c (in this case the solid is pure A).
The ratio of amount of liquid to solid is equal to the ratio of the lengths ac/ab.

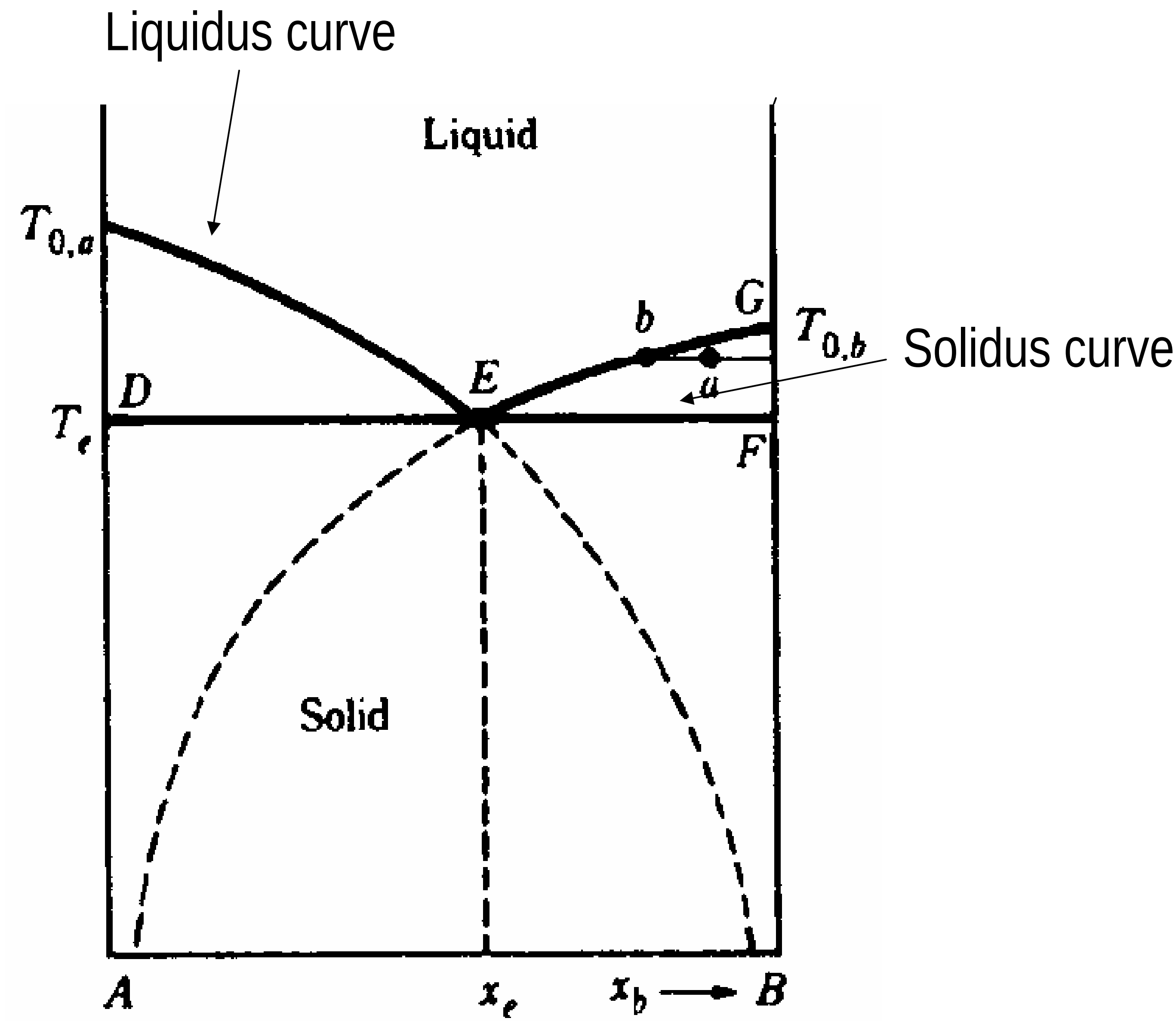


This curve does not represent the situation over the entire region of composition. At larger mole fractions of B, solid B separates out.
If the solution is ideal, the same law holds good for the pure substance, B.
In this case,

$$\ln x_B = - \Delta H_{fus,B}/R\ (1/T – 1/T_{0B}),$$

At temperature T_e both the curves meet and this is the minimum in temperature that can be reached by the system with solid A, B and solution in equilibrium. This temperature is called the eutectic temperature. At this point, F' = 3 – P = 3 – 3 = 0, the system is invariant at this temperature. If heat is removed from the system, the three phases will be in equilibrium. The relative amounts of phases will change depending on the heat flow into the system.

The total phase diagram is represented in the diagram (b).
The line DEF is the solidus curve. Below this line only solid A and B exist. The ideal system depicted in (a) is also shown.



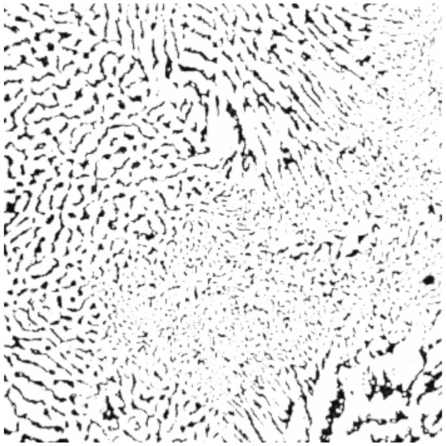
Solid-liquid equilibrium in a two component system.

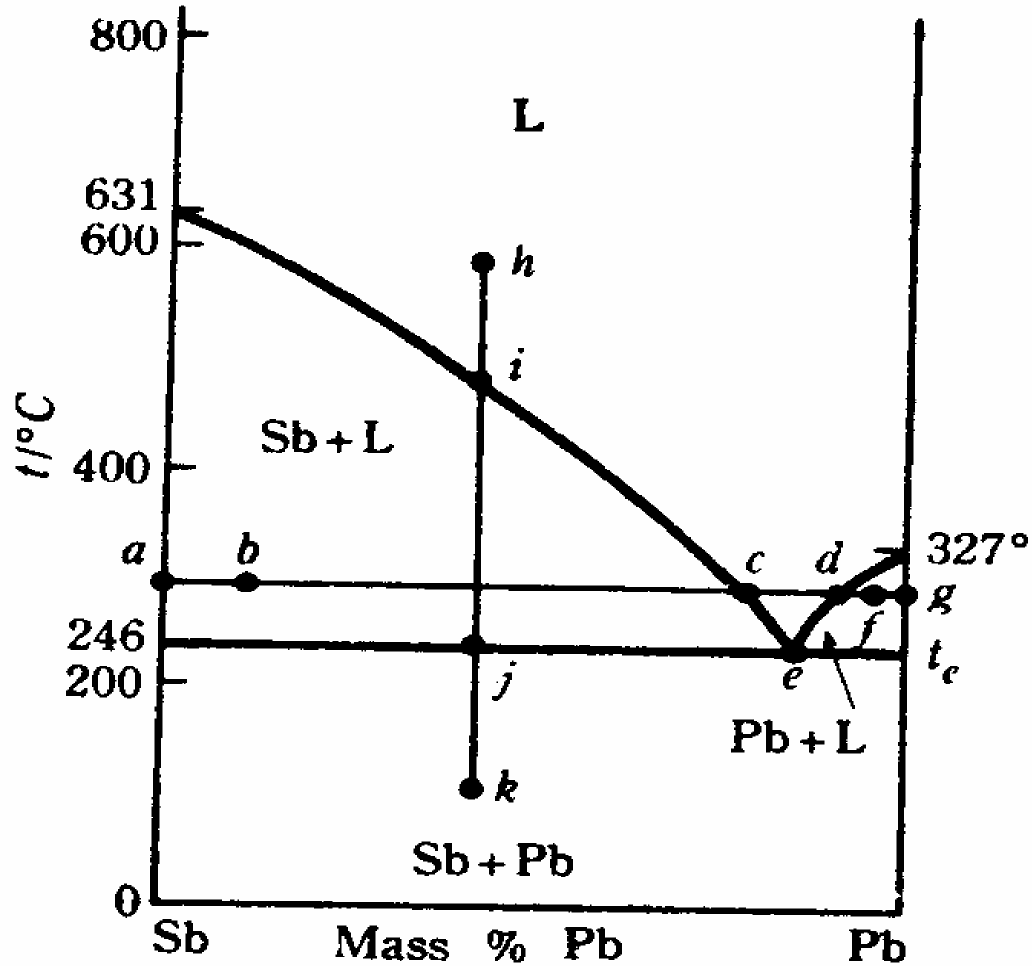
The lead-antimony system is a simple eutectic system. This is shown below as an example. The various temperatures are shown in the graph. The line hijk is called an isopleth, representing constant composition. This represents the changes in the system as the temperature is varied.

It was thought that at this temperature what is melted is a compound. But microscopic analysis showed that these are isolated crystals of A and B in the system.

In systems such as lead-antimony which form alloys, the grains of A and B are much smaller, yet the two phases remain. In aqueous systems, this eutectic mixture is called a cryohydrate and the eutectic point is called the cryohydric point.

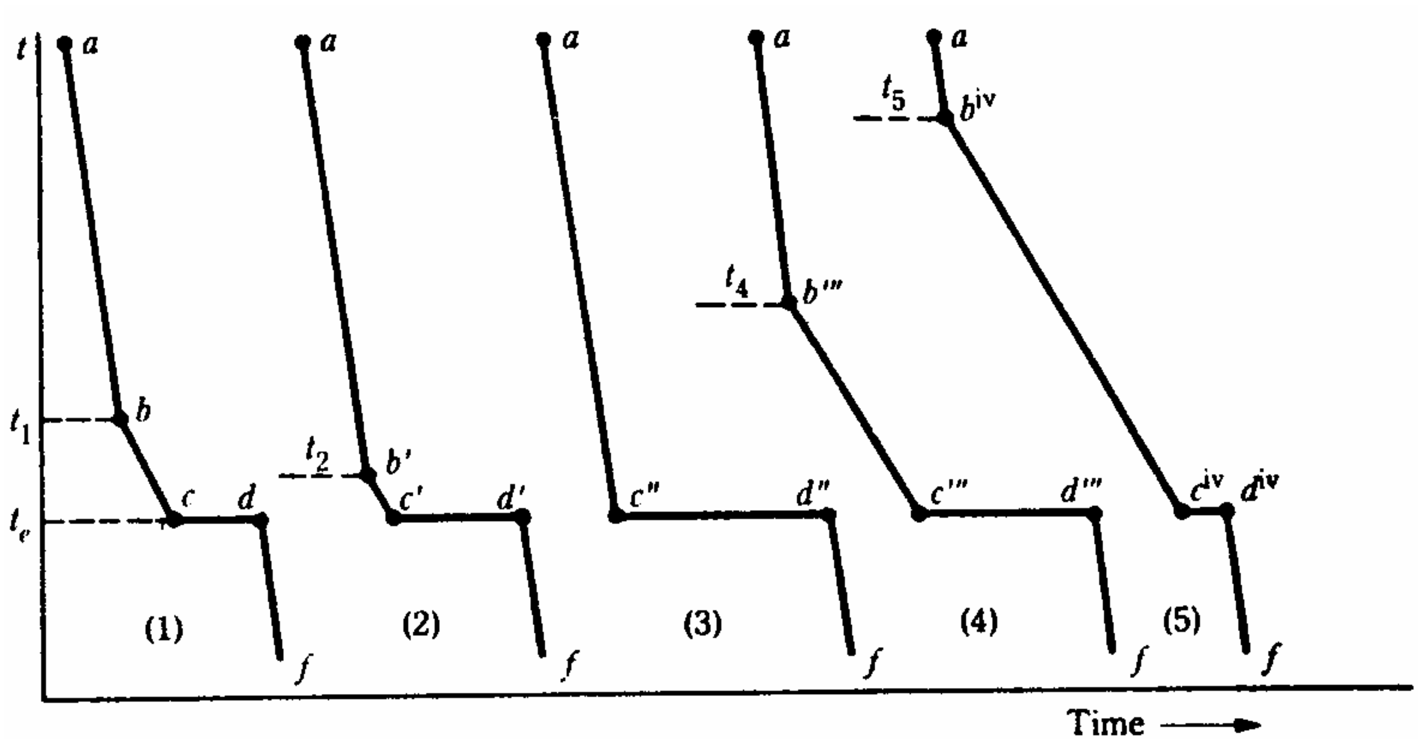
Micrograph of eutectic Pb-Sn alloy showing a fine mixture of Pb-rich and Sn-rich phases





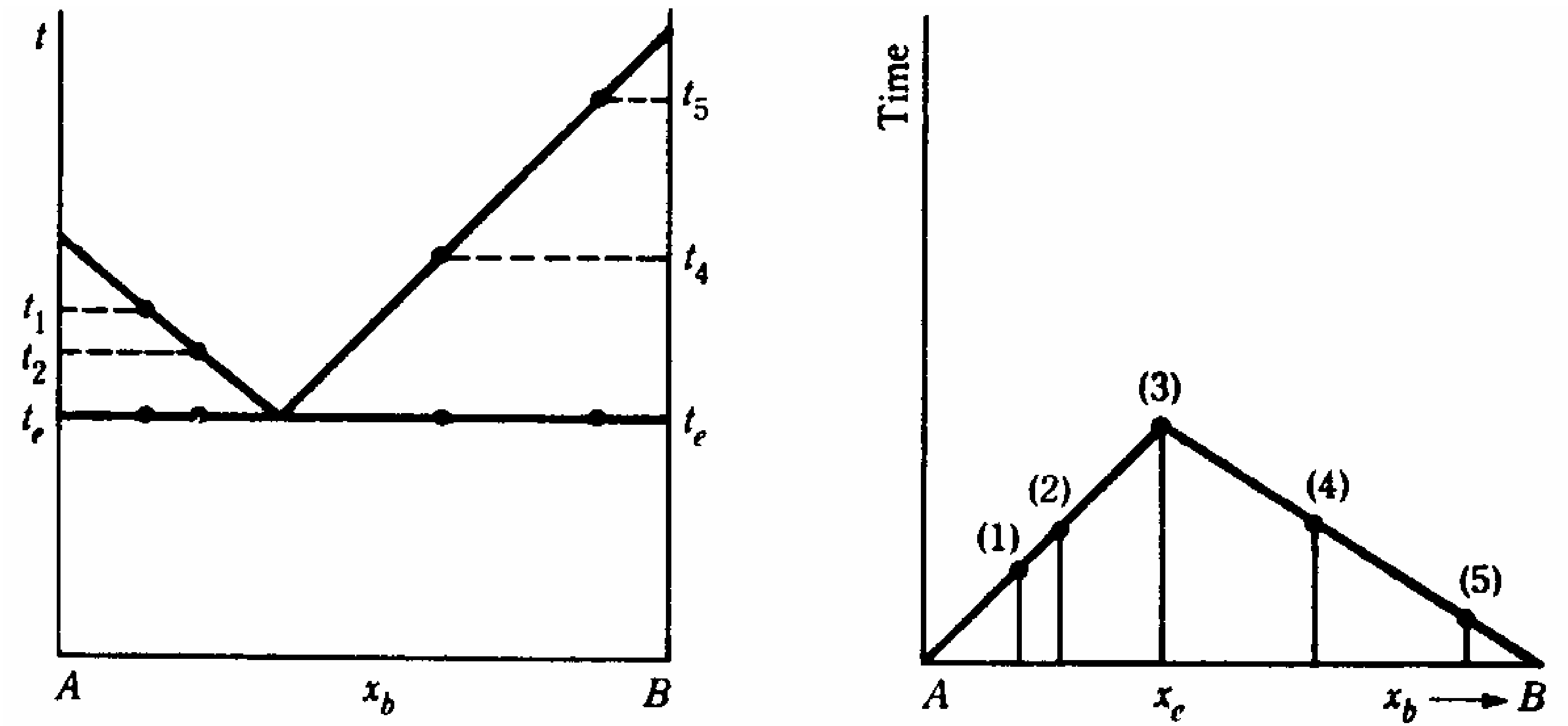
Lead-antimony system

The phase diagram can be studied using cooling curves. A series of compositions are taken at a temperature above the melting points of A and B. The mixture is allowed to cool. The temperature is noted as a function of time. The cooling curve is plotted as given below.



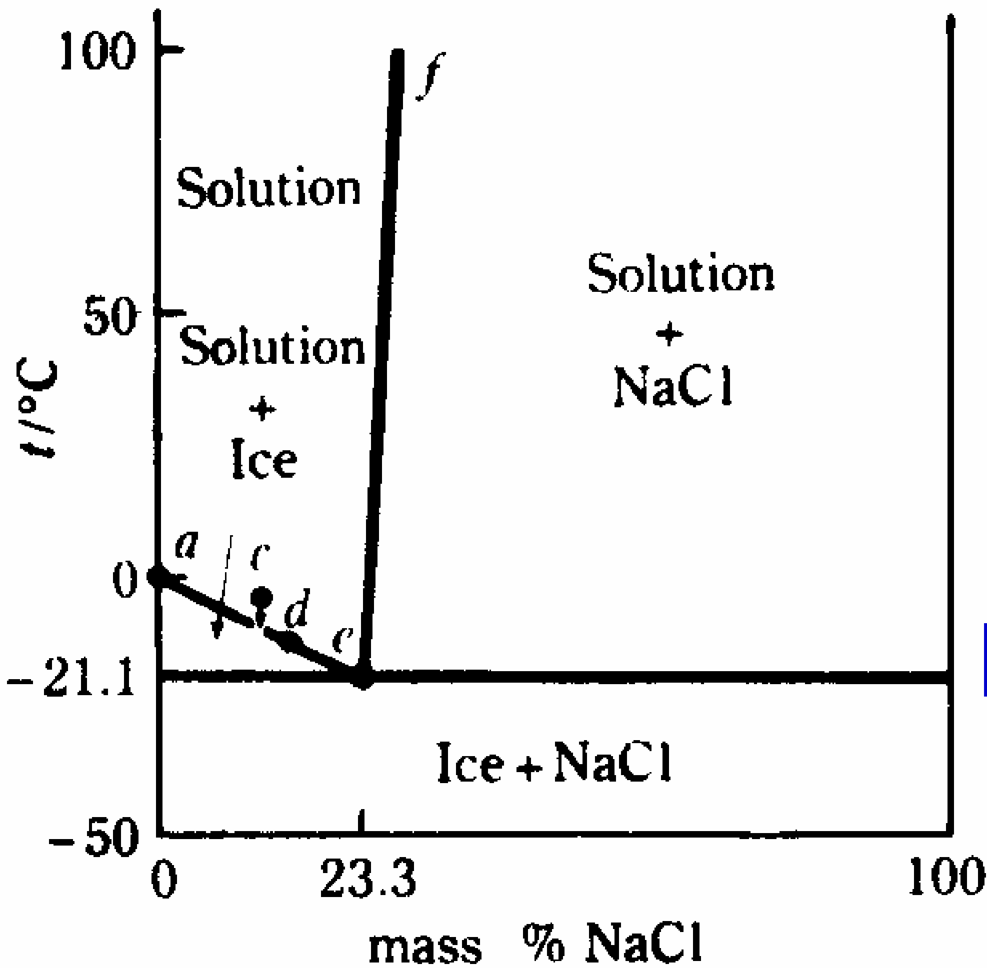
Cooling curves

The two points at which the slope changes correspond to the melting point of the mixture and the eutectic point. In composition marked (3) no melting point is noted only the eutectic point is observable.
The horizontal plateau is called the eutectic halt. This increases as the composition is closer to eutectic composition. The phase diagram can be drawn by using either of the data. The eutectic point can be found out by plotting the eutectic halt as a function of composition.



Eutectic halt as a function of composition

The freezing mixture



NaCl/water system

The eutectic compositions for several freezing mixtures are given below.

Salt	Eutectic temperature C	Mass percent anhydrous salt in eutectic
Sodium chloride	-21.1	23.3
Sodium bromide	-28.0	40.3
Sodium sulfate	-1.1	3.84
Potassium chloride	-10.7	19.7
Ammonium chloride	-15.4	19.7

Eutectic system with compound formation