Unit-4 Phase Rule

PHASE RULE: For the study of the behavior of the heterogeneous systems an important generalization was put forward by American Physicist Willard Gibbs in 1874. This generalization commonly known as **'phase rule'** is applicable to all heterogeneous systems in equilibrium without any exception. This rule cannot be expressed on hypothetical assumptions. This rule cannot be expressed in words. However, it may be stated mathematically as follows:

$$F= C-P+2$$

Where,

F is the number of degree of freedom,

C' is the number of component

P is the phases of the system.

When a heterogeneous system in equilibrium at a definite temperature and pressure, the number of degrees of freedom is equal to by 2 the difference in the number of components and the number of phases provided the equilibrium.

For understanding the various applications of phase rule a clear understanding of the various terms, phases (P), components (C) and degrees of freedom (F) present in the phase rule, is essential which have their specific meanings.

DEFINITION OF THE TERMS USED IN PHASE RULE

Phase (P):
A phase is defined as "an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces"
Example:

i. Liquid phase: The number of liquid phase depends on the number of liquids present and their miscibility.

i) If two liquids are immiscible, they will form two separate liquid phases.
Example: benzene and water

ii) If two liquids are miscible they will form one liquid phase only.

ii. Solid phase: Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it.
Example: Many forms of sulphur can exist together, but these are all separate phases.

iii. Gaseous phase: Since a gaseous mixture is thoroughly miscible in all proportions, it will form one phase only. Example: a mixture of N2 and H2 forms one phase only.

Components (C):

The minimum numbers of independently variable constituents in terms of which the composition of each phase of a heterogeneous system can be expressed directly or in the form of a chemical equation are called the components of system (C).

For example, a system consisting of a solution of sugar in water (P = 1 i.e. solution phase) is a two-component system because the solution phase present in the system consists of two constituents—water and sugar.

Some common examples related to the components are as follows:

Consider the following system consisting of ice, water and vapour in equilibrium.

$$\text{Ice (s)} = \text{Water (l)} = \text{Vapour (g)}$$

The system consists of three phase's ice, water and vapour phase. The chemical substance present in each phase is H2O. Therefore, the composition of each phase is expressed in terms of H2O. Hence, it is called one-component system.

Degree of Freedom (F):

The smallest numbers of independently variable factors such as temperature, pressure and concentration which must be required in order to define the system completely are called the degree of freedom. Degree of freedom of a system is also known as variance.

When a system having no degree of freedom

F = 0 it is called non-variant system or invariant system.

When a system having only one degree of freedom

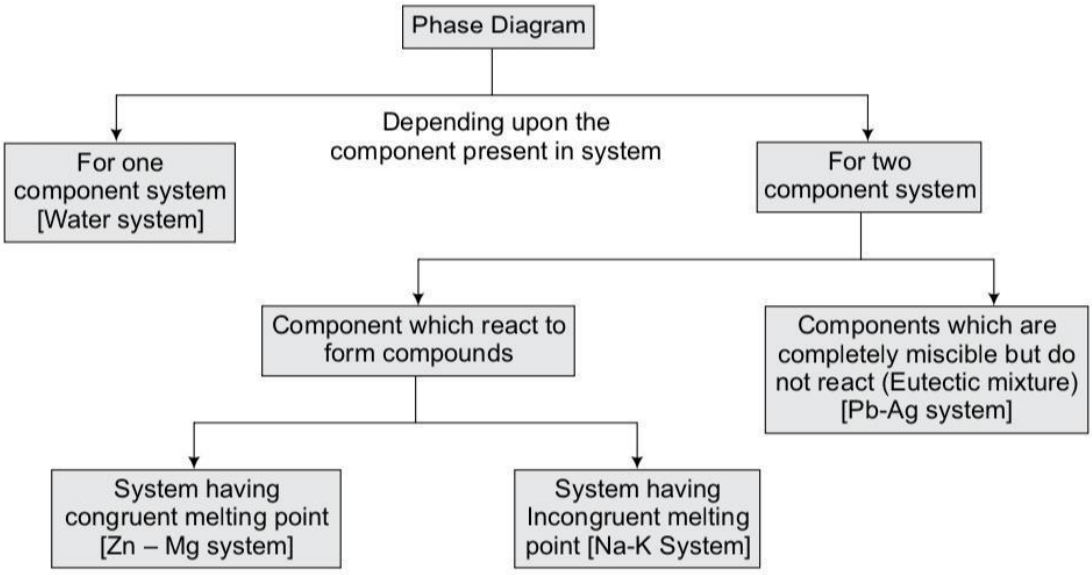
F = 1 it is a univariant or a monovariant system.

Similarly, a system having two degrees of freedom

F = 2 is a bivariant system and so on.

PHASE DIAGRAMS:

The graphical presentation giving the conditions of pressure and temperature under which the various phases are existing and transform from one phase to another is known as the phase diagram of the system. A phase diagram consists of areas, curves or lines and points.



PHASE RULE FOR ONE – COMPONENT SYSTEMS:

The least number of phases possible in any system is one. So, according to the phase rule equation, a one-component system should have a maximum of two degrees of freedom.

When C = 1, P = 1

So, F = C − P + 2 = 1 − 1 + 2 = 2

Hence, a one-component system requires a maximum of two variables to be fixed in order to define the system completely. The two variables are temperature and pressure. So, phase diagrams for one component system can be obtained by plotting Pressure vs Temperature.

In case of a one-component system, phase diagram consists of areas, curves or lines and points which provide the following information's regarding the system:

Point on a phase diagram represents a non-variant system.

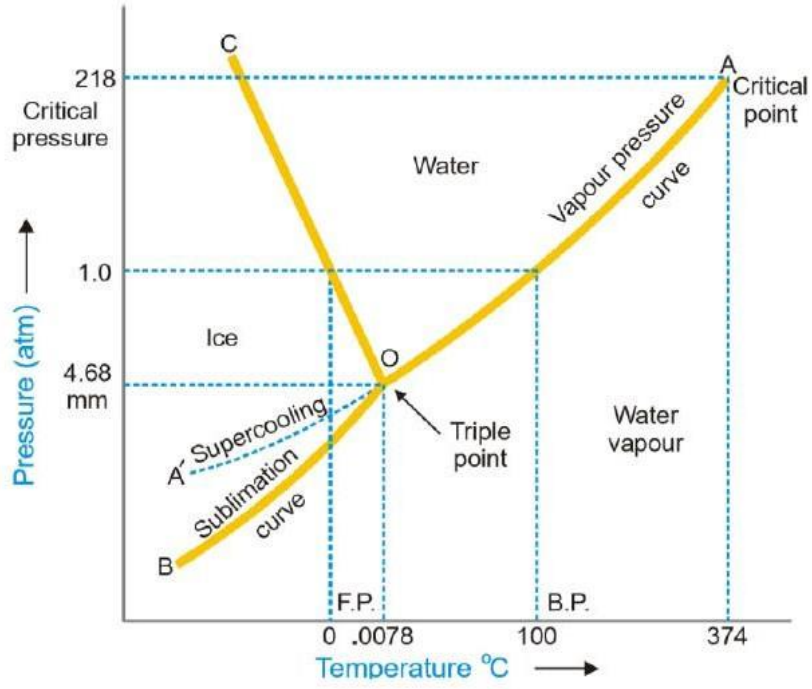
Area represents a bivariant system

Curve or a line represents a univariant system.

Water system and the sulphur system are the example of one component systems.

1. Water System: Under normal conditions the system 'water' is a three-phase, one-component system. The three phases involved are liquid water, ice, water vapour. All these phases can be represented by one chemical entity H_2O and hence one component of the system. The number of

phases which can exist in equilibrium any time depends on the conditions of temperature and pressure. The phase diagram or PT-graph of the system/ water/ice/vapour is shown in Fig. The salient features of the phase diagram are listed below.



Phase diagram of the water system

(1) The Curves OA, OB, OC

(2) The Triple Point O

(3) The Areas AOC, AOB, BOC

Let us proceed to discuss the significance of each of these features.

(1) The Curves OA, OB, OC

These three curves meet at the point "**O"** and divide the diagram into three regions or areas.

i) Curve OA, the Vapour Pressure curve of Water: It represents the vapour pressure of liquid water at different temperatures. The two phase's water and water vapour coexist in equilibrium along this curve. The curve OA terminates at A, the critical point (218 atm, temp. 374ºC) when the liquid and vapour are indistinguishable from each other and there is left one phase only. When the vapour pressure is equal to one-atmosphere, the corresponding temperature, as indicated on the phase diagram is the boiling point (100ºC) of water.

ii) Curve OB, the Sublimation curve of Ice: It shows the vapour pressure of solid ice at different temperatures. The two phases solid ice and vapour coexist in equilibrium along this curve. At the lower limit the curve OB terminates at absolute zero (– 273ºC) where no vapour exists.

iii) Curve OC, the Fusion curve of Ice: It depicts the effect of pressure on the melting point of ice. Here ice and water coexist in equilibrium. The fact that OC slopes to the left indicates that the melting point of ice decreases with increase of pressure. Since ice melts with decrease in volume by Le Chatelier's principle the melting point is lowered by an increase of pressure. It may be noted that the 1.0 atmosphere line meets the fusion curve at 0ºC which is the normal melting point of ice.

Along the curves OA, OB, OC there are two phases in equilibrium and one component.

Therefore,

$$F = C – P + 2 = 1 – 2 + 2 = 1$$

Has one degree of freedom i.e., is monovariant.

(2) The Triple point 'O' :

The curves OA, OB and OC meet at the triple point 'O' where all the three phases liquid water/ ice/vapour are in equilibrium. This occurs at 0.0076ºC and vapour pressure 4.58 mm Hg. Since there are three phases and one component, we have

$$F = C– P + 2 = 1 – 3 + 2 = 0$$

i.e., the system at the triple point is nonvariant. Thus if either pressure or temperature is changed, the three phases would not exist and one of the phases would disappear.

(3) Area AOC, AOB, BOC :

The areas or regions between the curves show the conditions of temperature and pressure under which a single phase–ice, water or vapour is capable of stable existence.

Thus, Area AOC represents conditions for the one-phase system water.

Area AOB represents conditions for the one-phase system water vapour.

Area BOC represents conditions for the one-phase system ice.

In all the three areas there being one-phase and one-component, we have

$$F = C – P + 2 = 1 – 1 + 2 = 2$$

Thus each system water, water vapour, or ice has 2 degrees of freedom i.e., the system is bivariant.

Reduced phase rule or condensed phase rule.

We know the phase-rule equation,

$$F = C - P + 2 \ldots\ldots\ldots (1)$$

For a two component system, C = 2 and hence the above equation becomes,

$$F = 2 - P + 2 = 4 - P \ldots\ldots\ldots (2)$$

The minimum number of phases in any system at equilibrium is one. It is clear from the equation (2) , the maximum number of degree of freedom is three.

Thus, three variables – pressure, temperature and composition of one of the components must be specified to describe the system. This will lead to three dimensional figures which cannot be conveniently represented on a paper. To make this simple, one of the three variables is kept constant.

In solid-liquid equilibrium of an alloy, practically there is no gaseous phase and the pressure will not have much influence. In the case of solid-liquid equilibrium, the experiments are generally carried out at constant pressure.

Thus the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a **condensed system.** This reduces the degree of freedom of the system by one. The phase rule equation is then written as

$$F' = C - P + 1 \ldots\ldots\ldots (3)$$

This equation is called **reduced phase rule or condensed phase rule.**

For a two component system the phase rule equation is written as

$$F' = C - P + 1$$

$$= 2 - P + 1 = 3 - P \ldots\ldots\ldots (4)$$

The above equation is known as the **reduced (condensed) form of phase rule for two component system.**

There are various types of solid-liquid equilibria of which only two of them are taken here.

1. Those equlibria in which the components are completely miscible with one another in liquid state. They do not form any compound on solidification. They give rise to merely an intimate mixture known as eutectic. Some examples of this system are

1) lead-silver system

2) Lead-Antimony system

3) Zinc-cadmium system

4) Potassium iodide- water system

2. Those equilibria in which the components enter into chemical combination. They give rise to one or more compounds. Examples of this system are :

1) Zinc-magnesium system

2) Calcium chloride – Potassium chloride system

3) Gold-Tellurium system

Silver – Lead System: This system has **two components** and **four phases.** The phases are: (i) solid silver; (ii) solid lead; (iii) solution of molten silver and lead; and (iv)vapour.

The boiling points of silver and lead being considerably high, the vapour phase is practically absent. Thus Ag/Pb is a condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore we need consider only the two remaining variables, namely the temperature (T) and concentration (C). The complete TC diagram of the system Ag/Pb is shown in Fig.

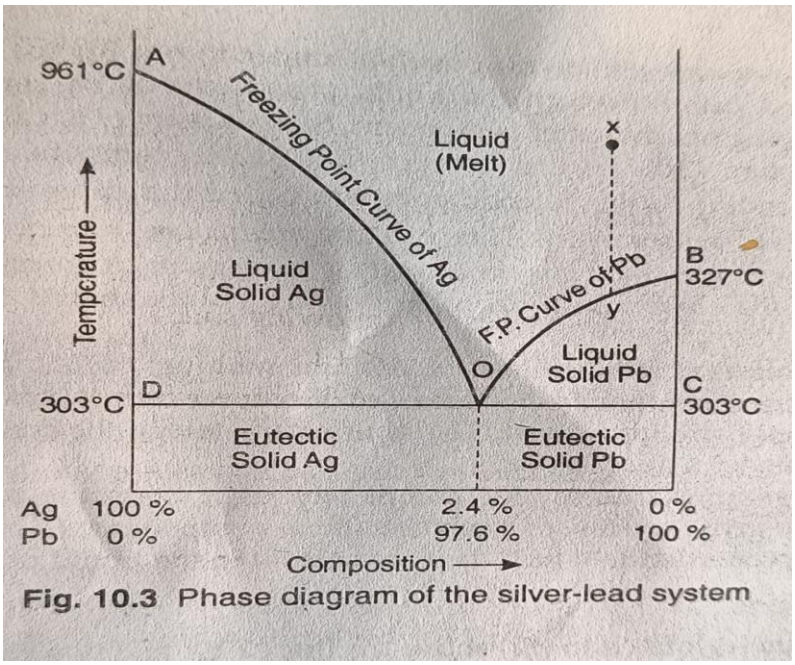


Fig. 10.3 Phase diagram of the silver-lead system

The salient features of the diagram are:

(a) Two curves, AO and BO

(b) Eutectic point, O

(c) Three areas: (i) above AOB; (ii) below AO; (iii) below BO

Curve AO; the Freezing point curve of Ag: A represents the freezing point or melting point of solid silver (961ºC) and the curve AO shows that the addition of lead lowers the melting point along it. The phases in equilibrium along AO are solid silver and solution of silver and lead. Applying the reduced phase rule equation

$$F' = C - P + 1$$

$$= 2 - 2 + 1 = 1$$ thus the system Ag/solution is monovariant.

Curve BO; the Freezing point curve of Pb: B represents the melting point of solid lead (327ºC) and the curve BO shows that the melting point is lowered by addition of silver. The phases in equilibrium along BO are solid lead and solution. The system is monovariant.

The Eutectic point O: The curves AO and BO intersect at O, which is called the eutectic point. Here three phases solid Ag, solid Pb, and solution are in equilibrium. Applying the reduced phase rule equation

$$F' = C - P + 1$$

$$= 2 - 3 + 1 = 0$$

Thus the system Ag/Pb/solution at O is nonvariant, Both the variables, temperature (303ºC) and composition (97.5% Pb, 2.5% Ag) are fixed. If you raise the temperature above the eutectic temperature, the solid phases Ag and Pb disappear and if you cool below it, you will land in the solid Ag/Pb area where solution phase is nonexistent.

The Area above AOB. This region represents the single phase system, the solution of molten Ag and Pb. Applying the reduced phase rule equation, we have

$$F' = C - P + 1$$

$$= 2 - 1 + 1 = 2$$ thus the system solution Ag/Pb is bivariant.

The area below AO represents the phases Ag + solution, while that below BO the phases Pb + solution. The area below the temperature 303º, represents solid Ag + solid Pb. All these areas have two phases and one degree of freedom,

$$F = C - P + 1$$

$$= 2 - 2 + 1 = 1$$

Desilverisation of lead:

Galena (PbS, an ore of lead) is usually associated with silver. During the extraction of lead from galena, a very small amount of silver (less than 0.1%) remains associated with lead because silver is soluble in lead to some extent. The lead thus obtained is known as argentiferous lead.

The process of removing these traces of silver from argentiferous lead is known as desilverisation of lead and is based on the phase diagram (Fig. 10.3) of silver-lead system.

The argentiferous lead is heated to a temperature well above its melting point so that the system consists only of liquid phase. Now let the point 'x' represents the system molten lead on the diagram in Fig. 10.3. It is then allowed to cool. The temperature of the melt will fall among the line xy without any change in concentration till the point y is reached. As soon as the point y is reached, lead will begin to crystallise out and the solution will contain relatively increasing amount of silver. Further cooling will shift the system along the line yo. Lead continues to separate out and is constantly removed by means of ladels. Thus the melt continues to be richer and richer in silver till the eutectic point 'O' is reached where percentage of silver increases to 2.4. This alloy containing 2.4% silver and 97.6% lead is treated for the recovery of silver profitably.

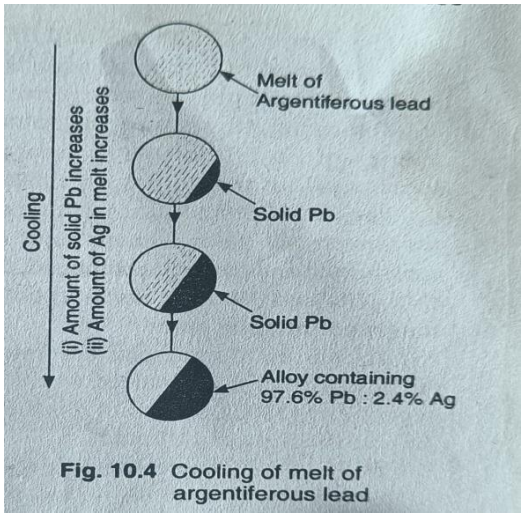


Fig. 10.4 Cooling of melt of argentiferous lead

The above principle of increasing the relative proportion of silver in the alloy is known as Pattison's process and is commercially used for the disilverisation of lead. The relative increase in the amount of solid lead and in the amount of silver in the residual melt on cooling is shown in fig 10.4.

Salt-Water System: ($NaCl+H_2O$)

The temperature-composition diagram of sodium chloride ($NaCl.2H_2O$) is shown in Fig 10.6. Neglecting the vapour phase, the system exhibits four phases: (i) $NaCl.2H_2O$ (ii) NaCl, (iii) ice and (iv) solution.

Let us study the various curves and points of the phase diagram.

(i) Curve AO: Point A is the melting point of ice (or freezing point of water) which is 0°C at 1 atmospheric pressure.

When sodium choride is added to water, its freezing point is lowered. Further, more and more freezing point of water is lowered by the addition of more and more sodium chloride. This takes place till point O is reached after which addition of NaCl does not lower the freezing point further. Thus the curve AO is called the freezing point curve. Along this curve two phases (ice and solution) are in equilibrium. Therefore, system along the curve is univariant which is also in accordance with the reduced phase equation.

$$F' = C - P + 1$$

$$=2-2+1=1$$

(ii) Curve OB: When further amount of sodium chloride is added at point O and the system is heated, ice disappears. The curve OB represents the effect of temperature on the solubility of the hydrated sodium chloride, NaCl 2H2O. Hence it is termed as the solubility curve of the hydrated sodium chloride. The steep rise of the curve OB shows that the solubility of sodium chloride increases slowly with rise is temperature. Along this curve two phase ($NaCl.2H_2O$ and solution) are in equilibrium and hence again the system is univariant.

$$F' = C - P + 1$$

$$=2-2+1=1$$

The point B ($0.15^{O}C$) represents the incongruent melting point of the dihydrate where anhydrous sodium chloride appears.

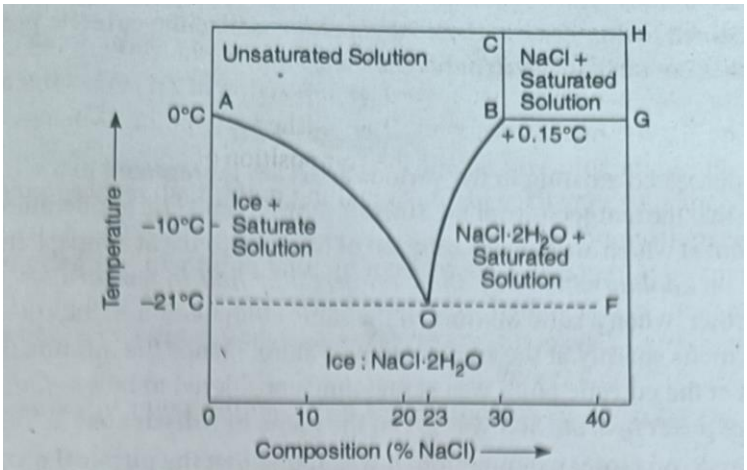


Fig. 10.6 Phase diagram of sodium chloride-water system

(iii) Curve BC: It is the solubility curve of the anhydrous sodium chloride. Here also two phases exist together. Hence the system along the curve BC is also univariant.

Point O: At point O the solution becomes saturated and the dihydrate, $NaCl.2H_2O$ separates out. Thus the system at the point O consists of three phases (ice, $NaCl.2H_2O$ and solution) in equilibrium. Solid as well as solution phase at this point contains 23% NaCl. The tempeature at this point (- 21^0C) is the lowest temperature that can be attained in this system. Hence this point is called the eutectic point. Since here three phases co-exist, the system here is invariant.

$$F' = C - P + 1$$

$$=2-3+1=0$$

The phases co-existing in the various areas are represented in the Fig. 10.6.

Congruent Melting Point:

A congruent melting point is the temperature at which a compound melts without decomposition or a change in composition. This means the solid and liquid phases of the substance have the same composition at the melting point.

Examples of Congruent Melting:

1. Sodium Chloride (NaCl): NaCl melts congruently at 801°C without decomposition.
2. Magnesium Oxide (MgO): MgO melts at 2852°C congruently.
3. Cesium Chloride (CsCl): CsCl melts congruently at 645°C into a liquid of the same composition.
4. Lead (II) Fluoride (PbF_2): PbF_2 melts at 824°C without breaking down.

Incongruent Melting Point:

Incongruent melting occurs when a solid compound melts into a liquid of different composition and a new solid phase. This means the original compound decomposes or reacts during melting, rather than forming a liquid with the same composition.

Examples of Incongruent Melting:

1. Potassium Feldspar ($KAlSi_3O_8$):

Instead of melting directly into a liquid, it decomposes into a liquid phase and a solid phase (leucite, $KAlSi_2O_6$).

2. Leucite ($KAlSi_2O_6$): Upon heating, it melts into a liquid and solid potassium feldspar.
3. Calcium Carbonate ($CaCO_3$): It decomposes to form calcium oxide (CaO) and carbon dioxide (CO_2) before melting.

4. Aluminum Silicates (like Al_2SiO_5 minerals – andalusite, sillimanite, kyanite)

They decompose into a liquid and a new solid phase rather than melting congruently.

Difference between Congruent and Incongruent Melting:

Congruent Melting: The solid melts directly into a liquid of the same composition.

Incongruent Melting: The solid decomposes into a liquid and another solid of different composition.

Freezing Mixtures:

A freezing mixture is a combination of substances that, when mixed, lower the temperature of the system by absorbing heat from the surroundings. These mixtures work by utilizing the principle of depression of freezing point, where the melting of a solid (such as ice) requires energy, causing a cooling effect.

Examples of Freezing Mixtures:

1. Ice and Salt (NaCl): One of the most common freezing mixtures, used in making ice cream. Salt lowers the freezing point of ice, causing it to melt and absorb heat.
2. Ice and Ammonium Chloride (NH_4Cl): This mixture produces a significant cooling effect and is used in some cooling applications.
3. Ice and Calcium Chloride ($CaCl_2$): Calcium chloride lowers the freezing point more than salt and is used in de-icing roads.
4. Dry Ice (CO_2) and Acetone: This mixture is used to achieve extremely low temperatures (as low as -78°C) for lab experiments.
5. Ice and Alcohol (Ethanol or Methanol): Alcohol prevents ice from forming a solid block, making it useful for cooling applications.

Applications of Freezing Mixtures:

1. Used in cooling and refrigeration.
2. Helps in ice cream making and food preservation.
3. Used in chemical and laboratory experiments requiring low temperatures.
4. Applied in medical cooling packs to reduce swelling or pain.