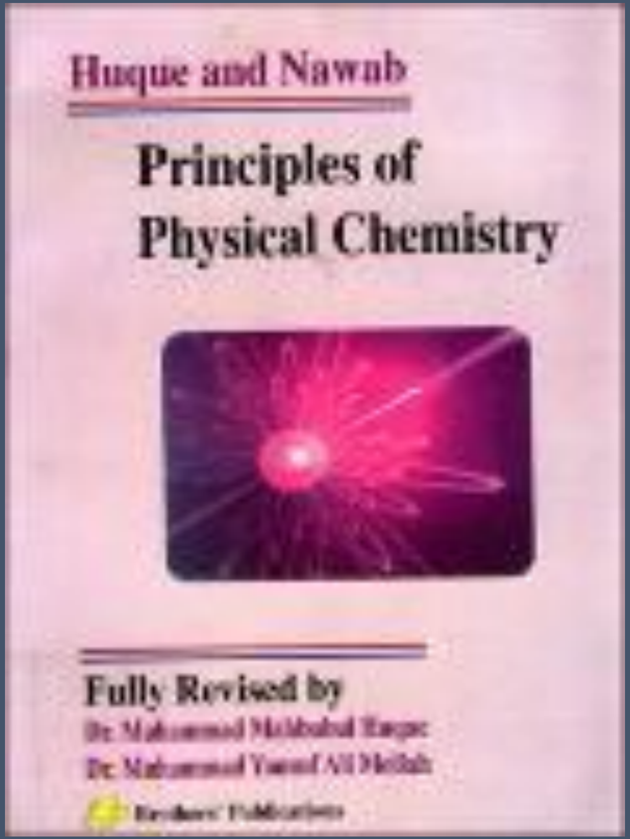
# Phase Rule and Phase Diagram



# Outlines

Phase equilibria

Phase rule

Component

Degree of freedom

Phase diagrams

# Phase Diagram

Phase rule : $F = C - P + 2$

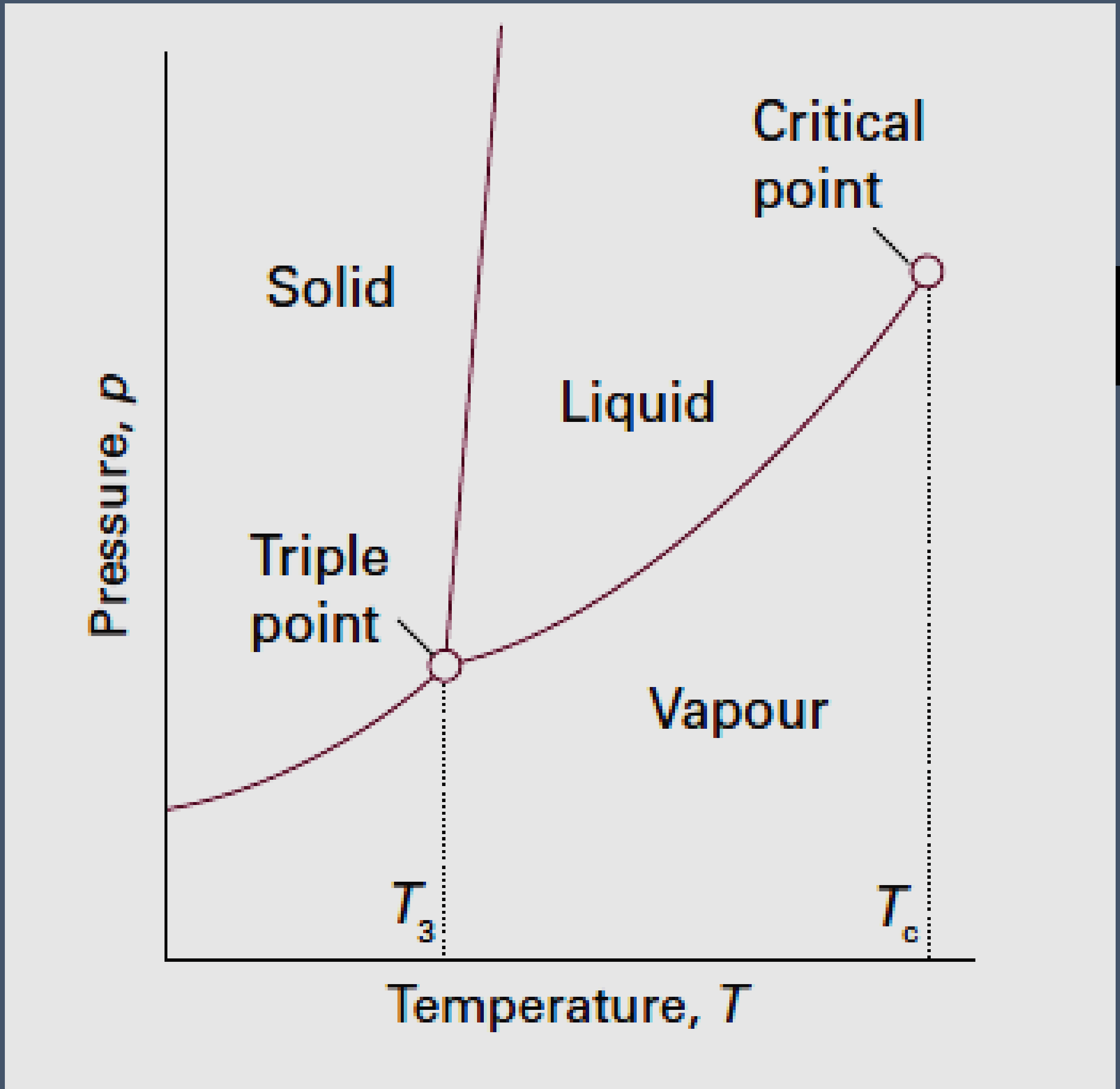
Vaporization melting (fusion), and the conversion of graphite to diamond are all examples of changes of phase without change of chemical composition.

**Phase diagram**

The conditions of equilibria between/among various phases of a substance can be presented on a single diagram…

Graph summarizes various phases that are in equilibrium

# A general phase diagram: One component system




M(*s*) $\rightleftharpoons$ M(*l*) $\rightleftharpoons$ M(*g*)

Make a list of characteristic features of this diagram ...

# Type of phase diagrams

## Phase rule : F = C – P + 2

*Independent variables: Pressure, temperature and concentration/composition*

### Based on number of components

- **Unary (one-component)**
- **Binary (two-component)**
- **Ternary (three-component)**

### Based on variables

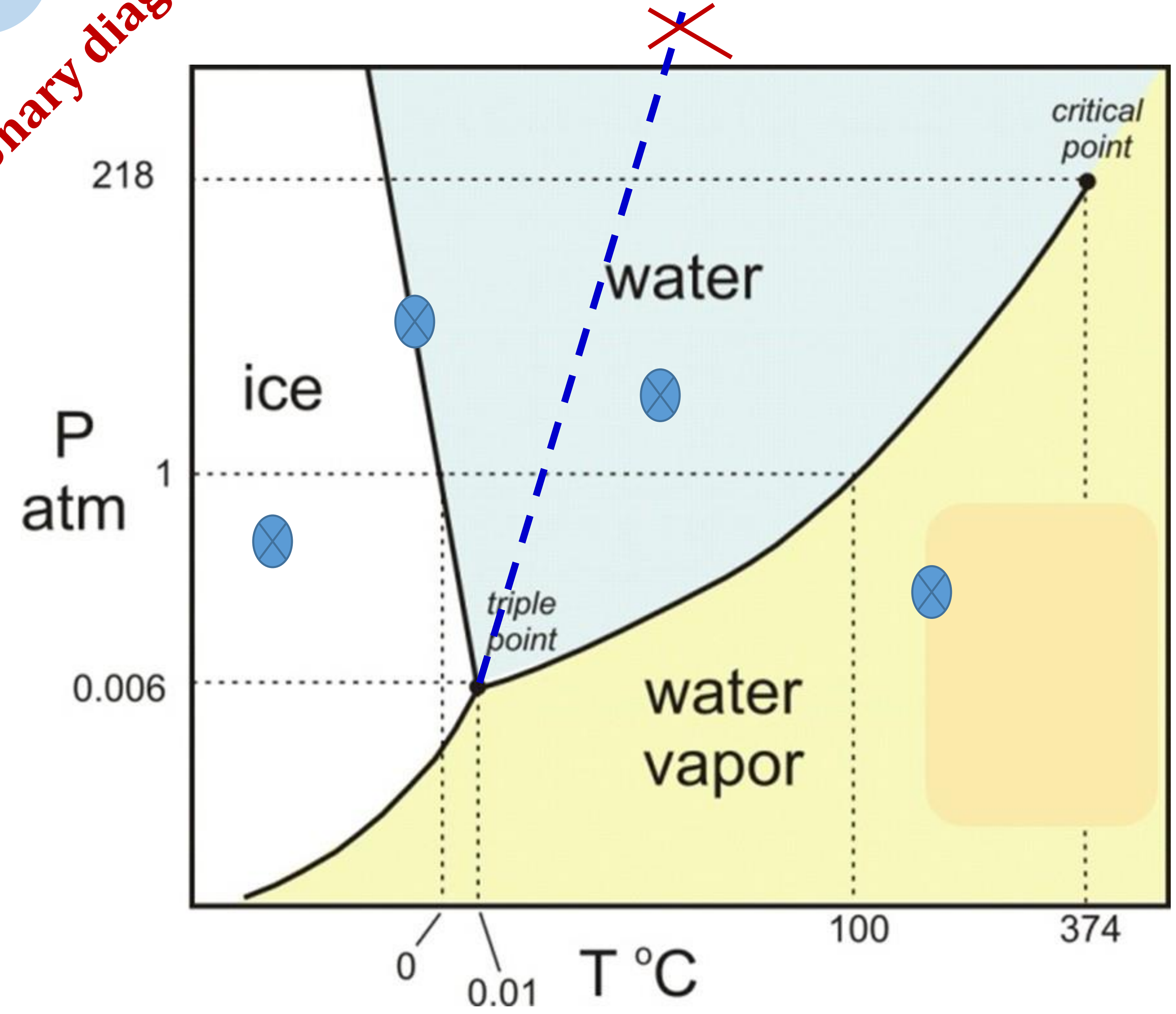
- **Pressure vs. Temperature (*p*-*c* diagram)**
- **Temperature vs. Composition (*t*-*c* diagram)**
- **Composition vs. Composition**

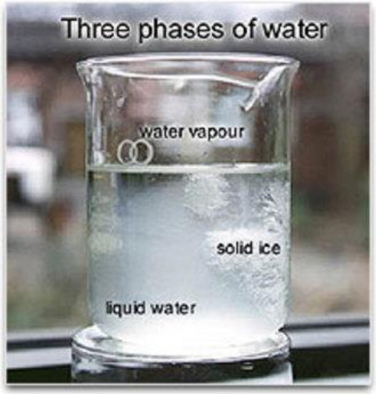
### Based on phases

- **Solid-Liquid-Gas**
- **Solid-Liquid**
- **Liquid-Liquid (immiscible)**
- **Liquid-Gas**
- **Solid-Solid**

# Phase Diagram of Water : One component system

Unary diagram




$$H_2O\ (s) \rightleftharpoons H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

**F = C – P + 2**

## Calculate F

**Along lines**

**Triple point**

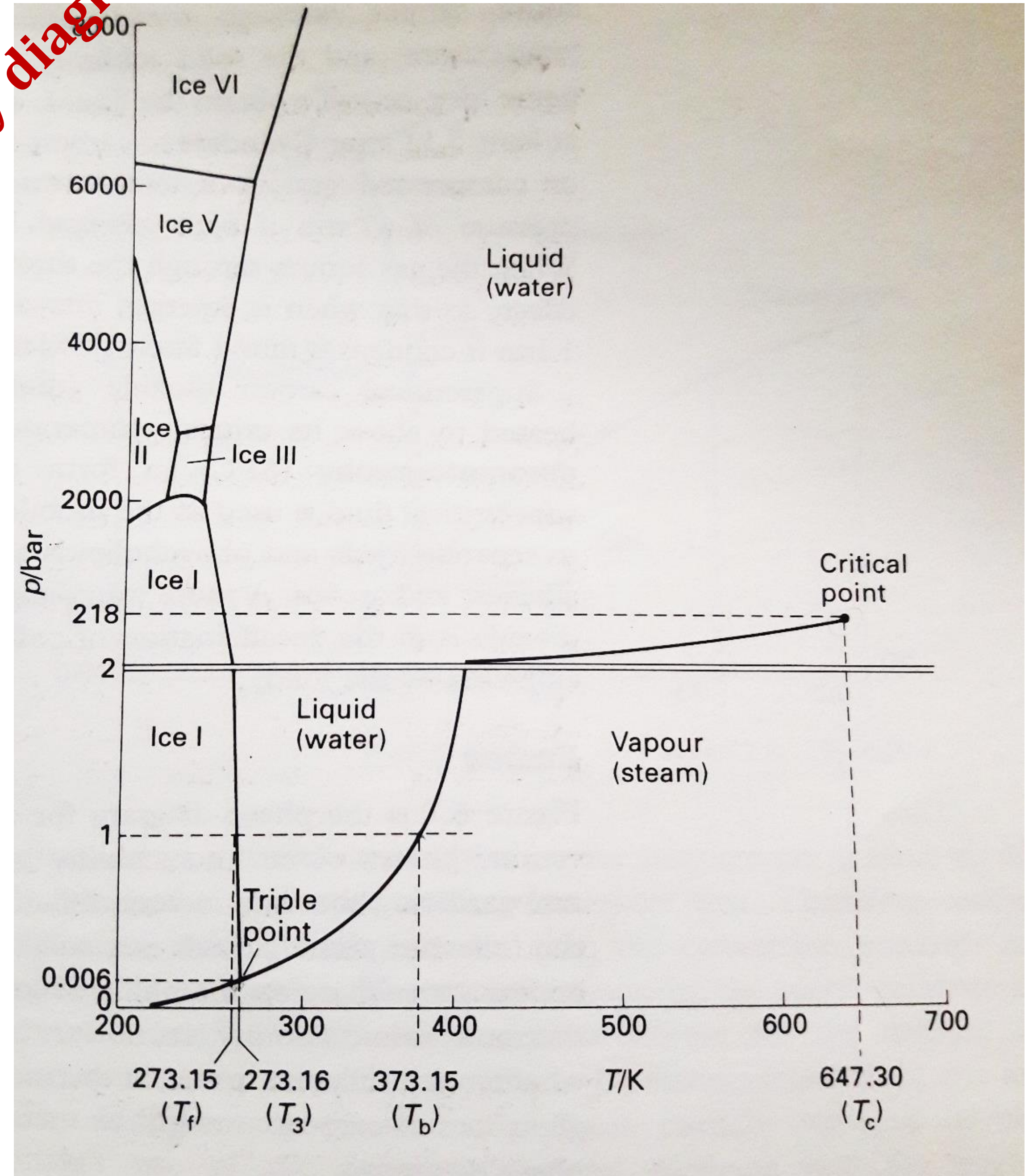
**Critical point**

**At points**

At any Triple Point, phase rule becomes:
F = 3-P = 3-3 = 0
(nonvarient)

# Phase diagram (of water): An important feature

Unary diagram




Closed box

# Clapeyron equation: Explanations for the nature of the lines

$S_m(s) < S_m(l) < S_m(g)$

$S_m$ : molar entropy

Line becomes more stepper

Slopes of boundaries

- solid-liquid
- solid-gas
- liquid-gas

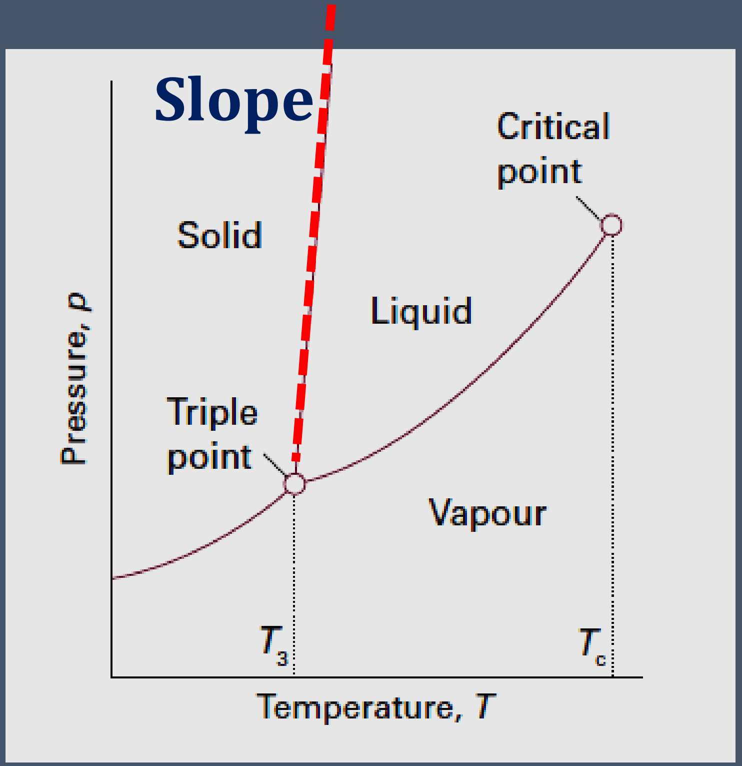
$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$

$$\frac{dp}{dT} = \frac{\Delta_{fus} H}{T \Delta_{fus} V}$$

Since,

$\Delta G = \Delta H - T\,\Delta S$

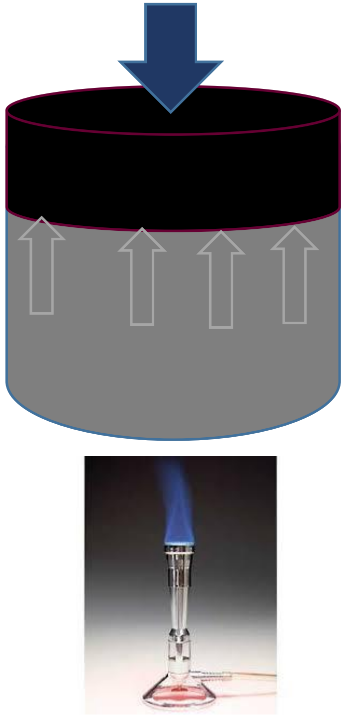
At equilibrium, $\Delta G = 0$

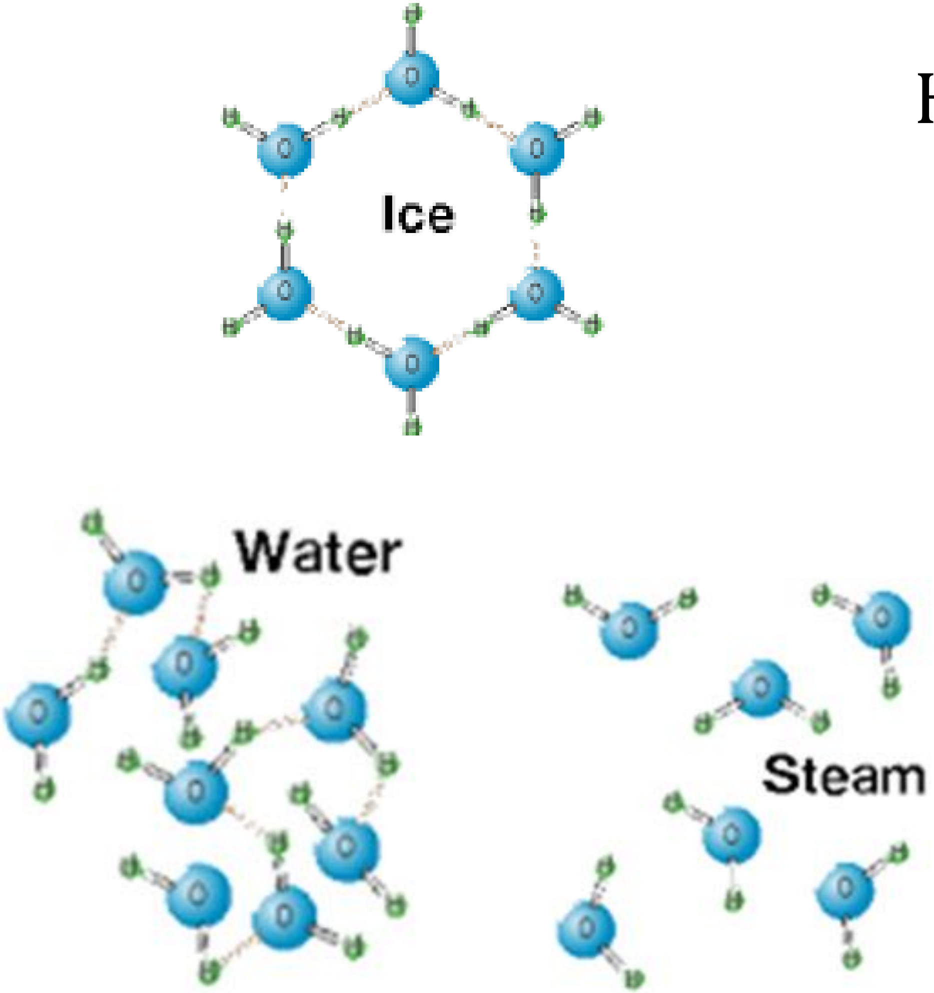


# Peculiar behavior of water

$$X(s) \rightleftharpoons X(l)$$

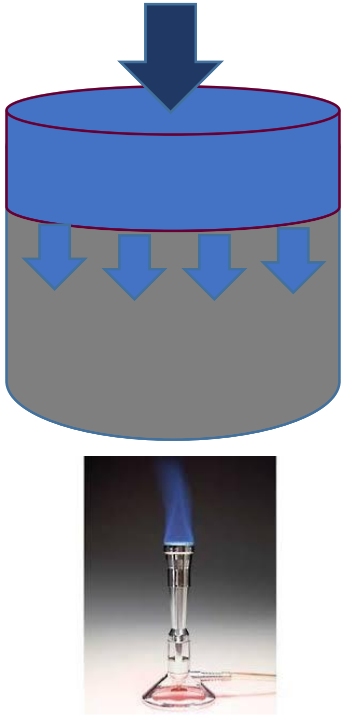
$$V(s) < V(l)$$





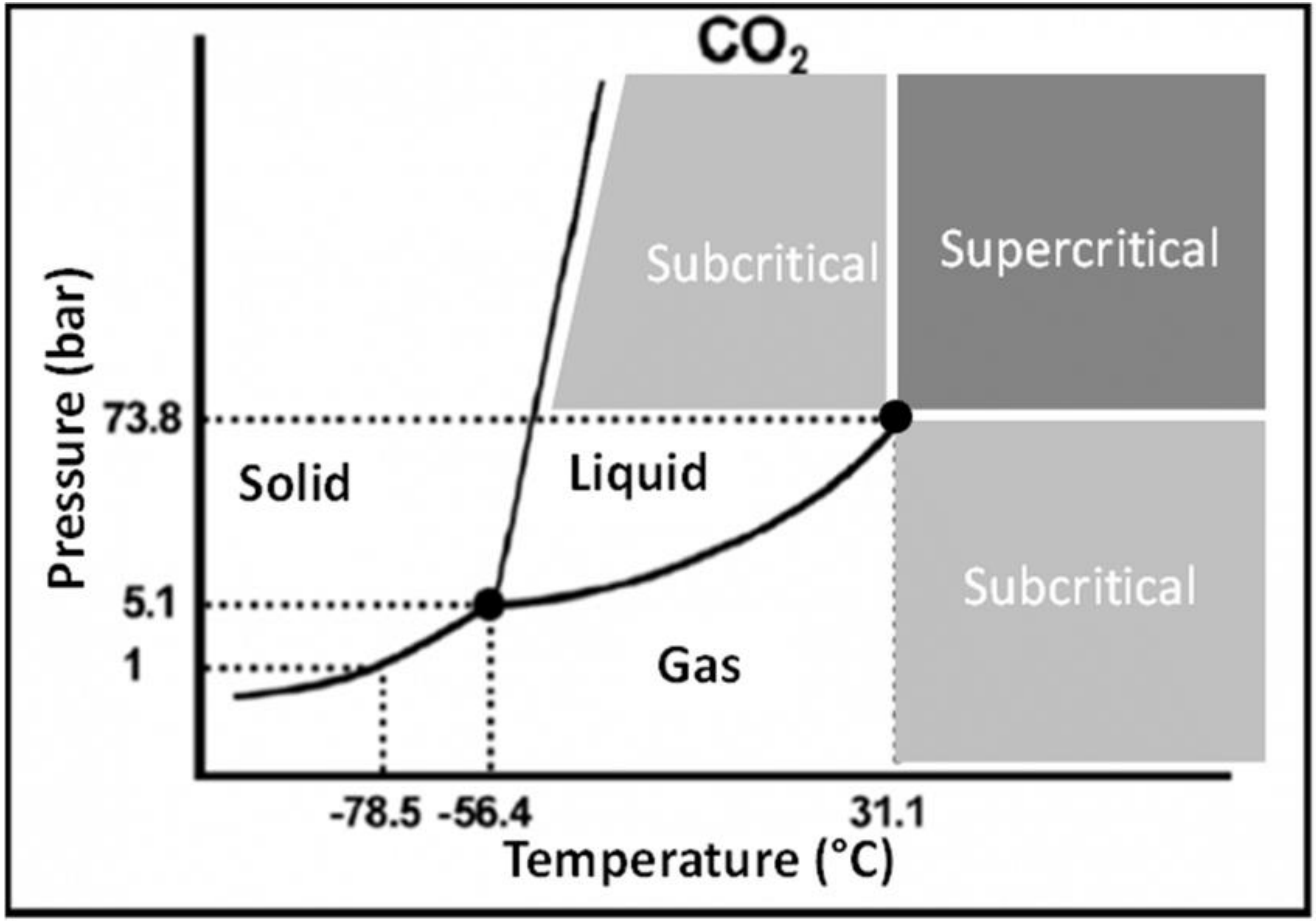

$$H_2O(s) \rightleftharpoons H_2O(l)$$

$$V(s) > V(l)$$



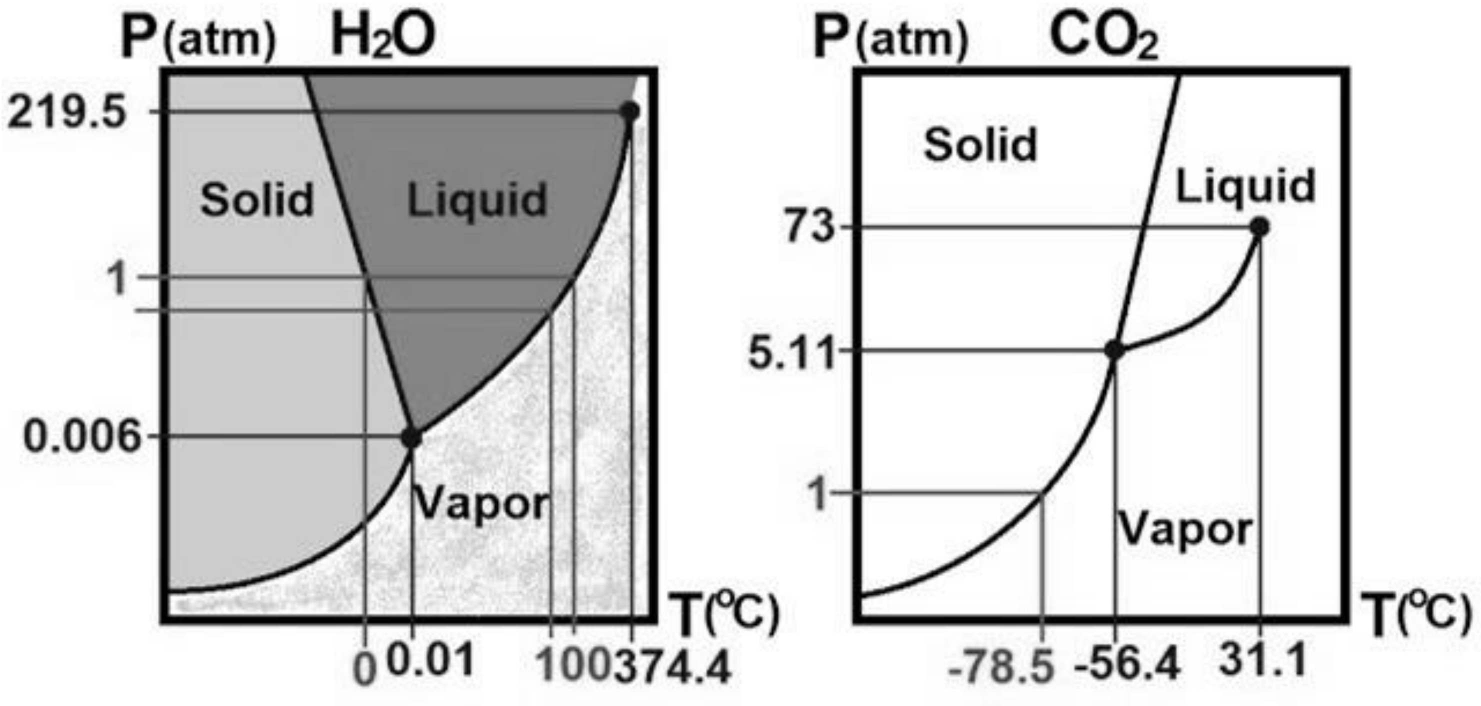
Unary diagram

# Phase diagram of $CO_2$



Unary diagram

# Phase diagram : Water vs. $CO_2$




(Ice vs. Dry ice)

**The triple point of water is 0.01 °C and 0.00604 atm**

**The triple point of $CO_2$ is -56.6 °C and 5.11 atm**

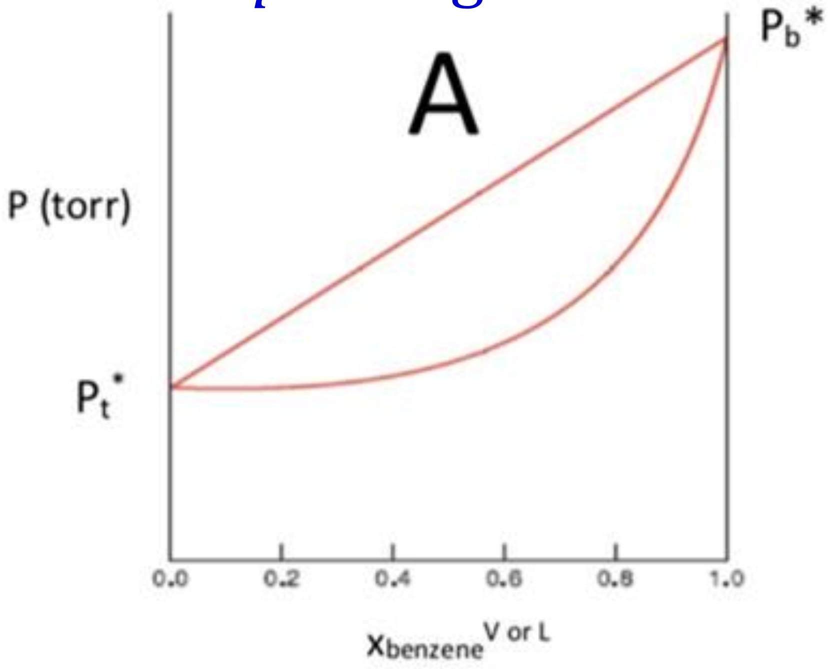
***Due to triple point pressure of $CO_2$ being above atmospheric pressure, solid $CO_2$ (dry ice) sublimes directly into a gas at normal atmospheric conditions, unlike water which can melt into a liquid.***

Binary diagram

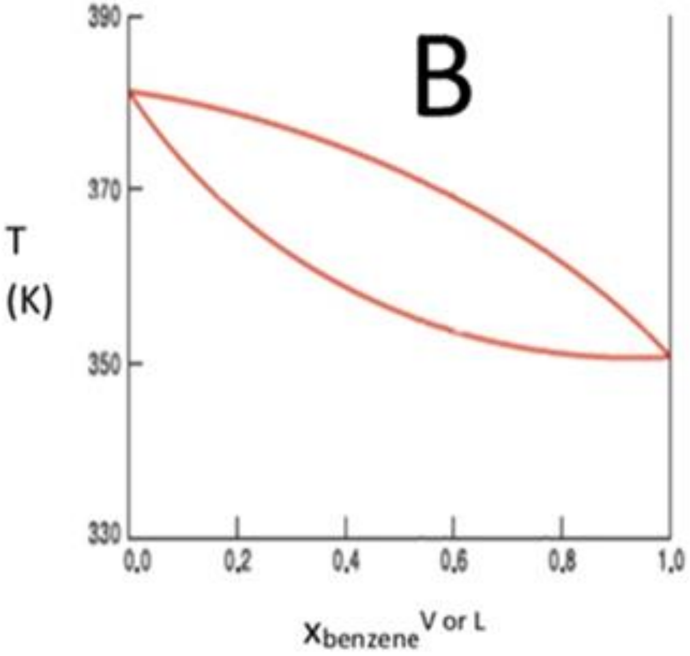
# Liquid-gas binary system (miscible)

*Benzene - Toluene*

*p-c* diagram




*t-c* diagram




Liquid – Vapour phase diagrams of binary solutions are drawn to illustrate the composition in the liquid and vapour phases of the two volatile components. The diagrams below show this for the binary mixture of benzene and toluene, which form a nearly ideal binary solution: (**A**) as a function of Pressure, at 23°C and (**B**) as a function of temperature at P = 1 atm. The x-axis gives x(benzene).

# Liquid-liquid binary system (immiscible)

*Aniline - Hexane*

## *t*-*c* diagram

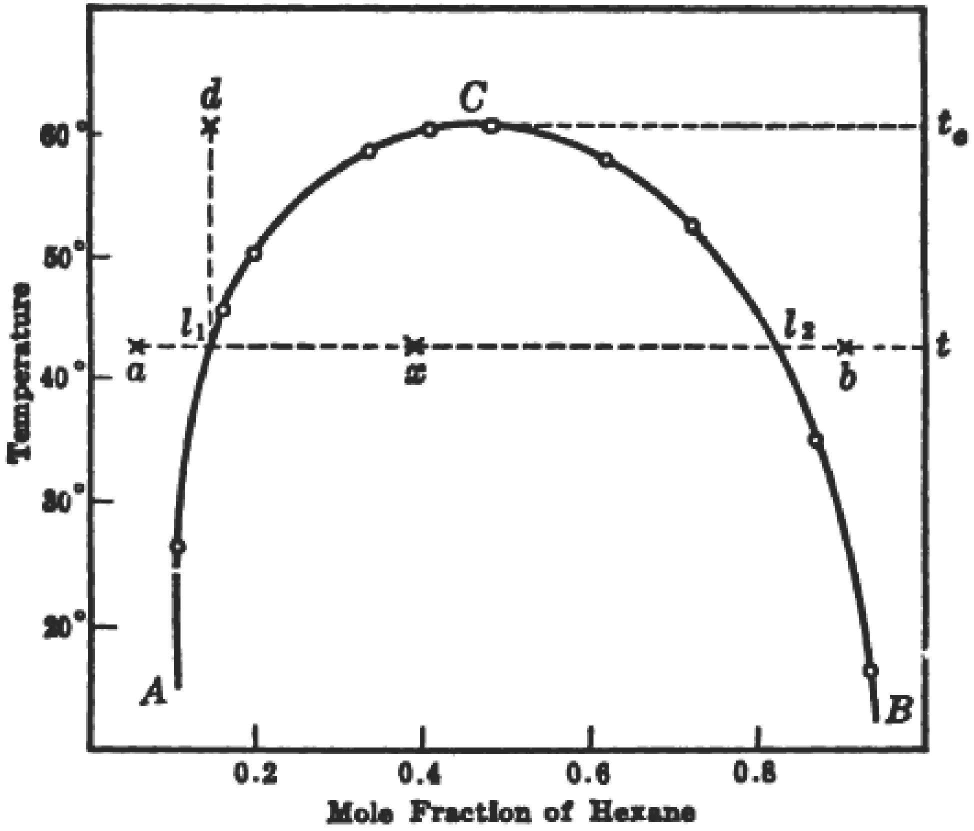
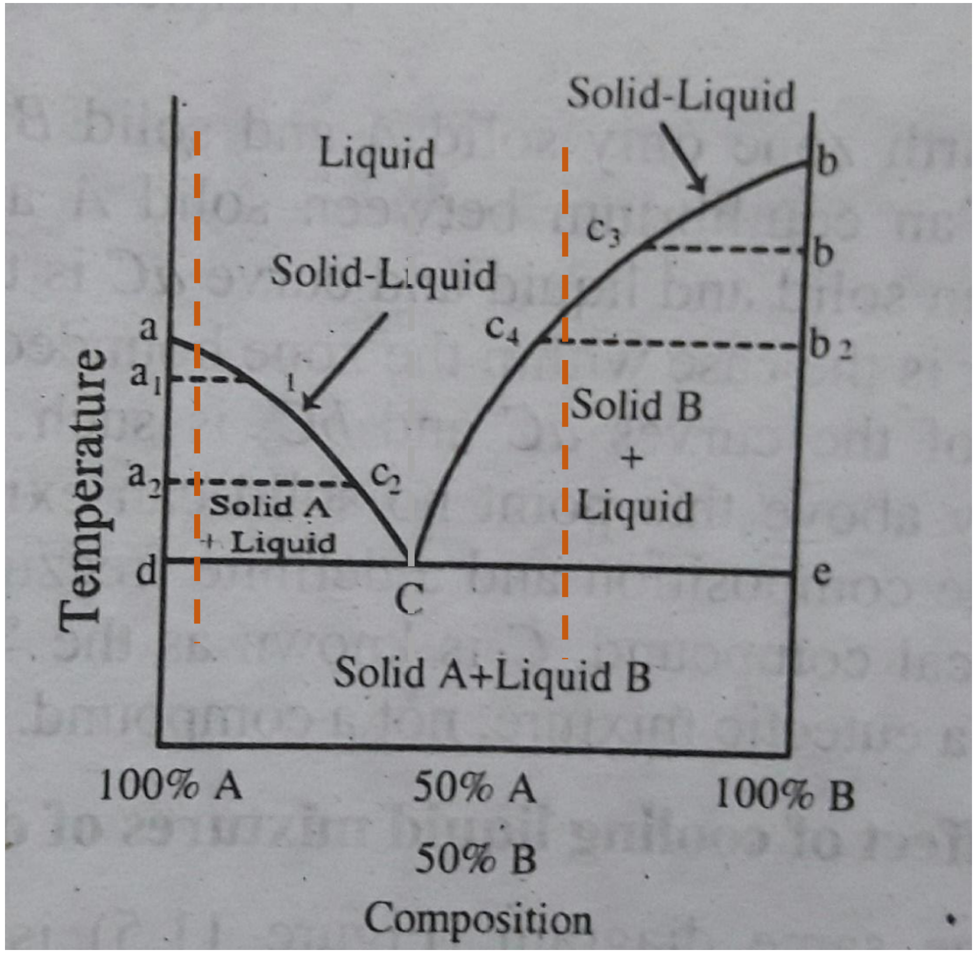



FIG. 39.10. Partially miscible liquids: the aniline-hexane system at atmospheric pressure

Binary diagram

# Solid-liquid binary system

## *t-c* diagram




*t-c* diagram

System:

A + B → no product (non-reacting system)

Liquid, A and liquid, B are miscible

Solid, A and solid, B are miscible

*Characteristics of t-c diagram:*

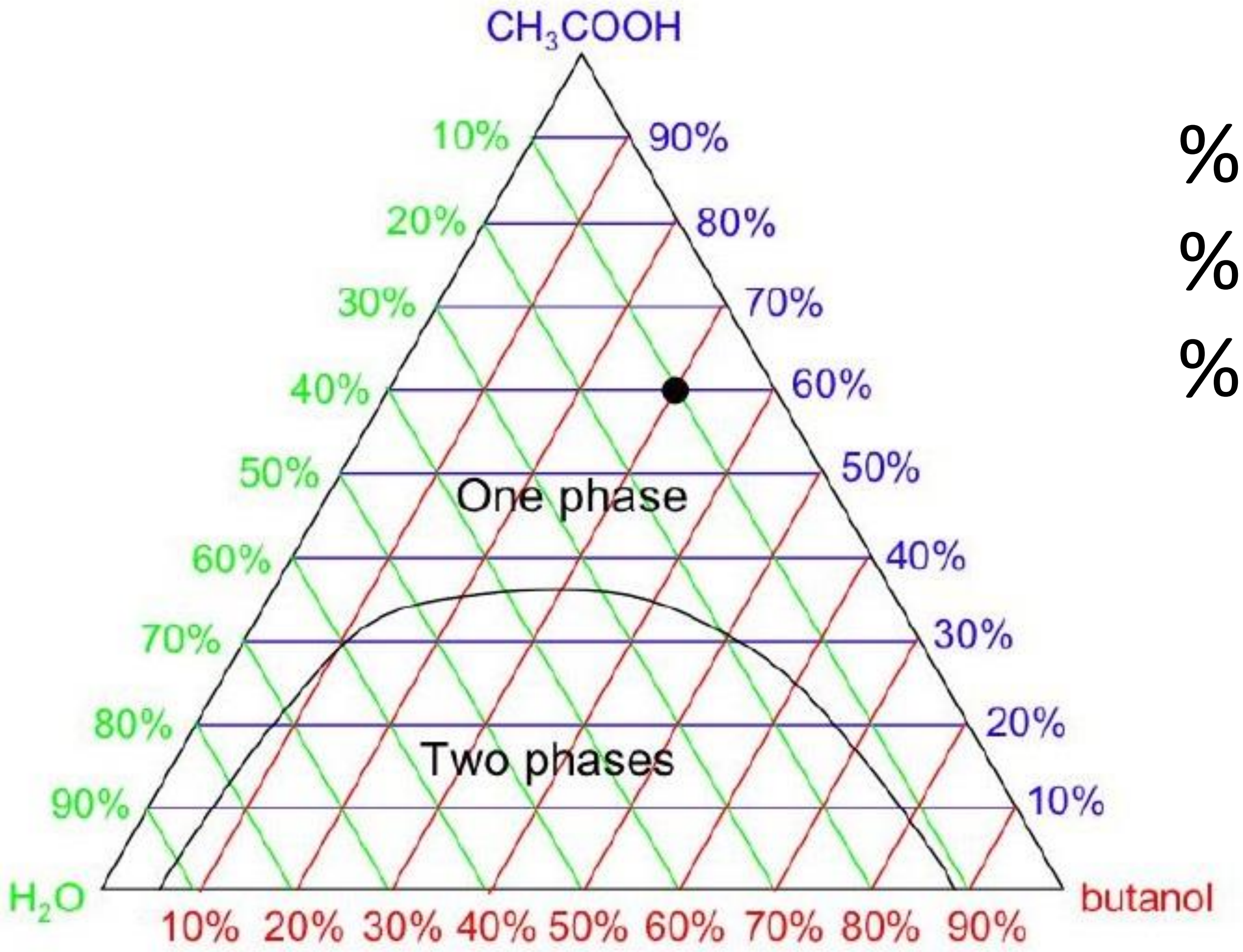
Point C: eutectic point

Areas: aCd, bCe, above aCb lines, below dCe line

Lines: aC, Cb, dCe line and dotted lines

F = C – P + 1 (condensed system)

# Ternary phase diagram : Liquid-liquid system



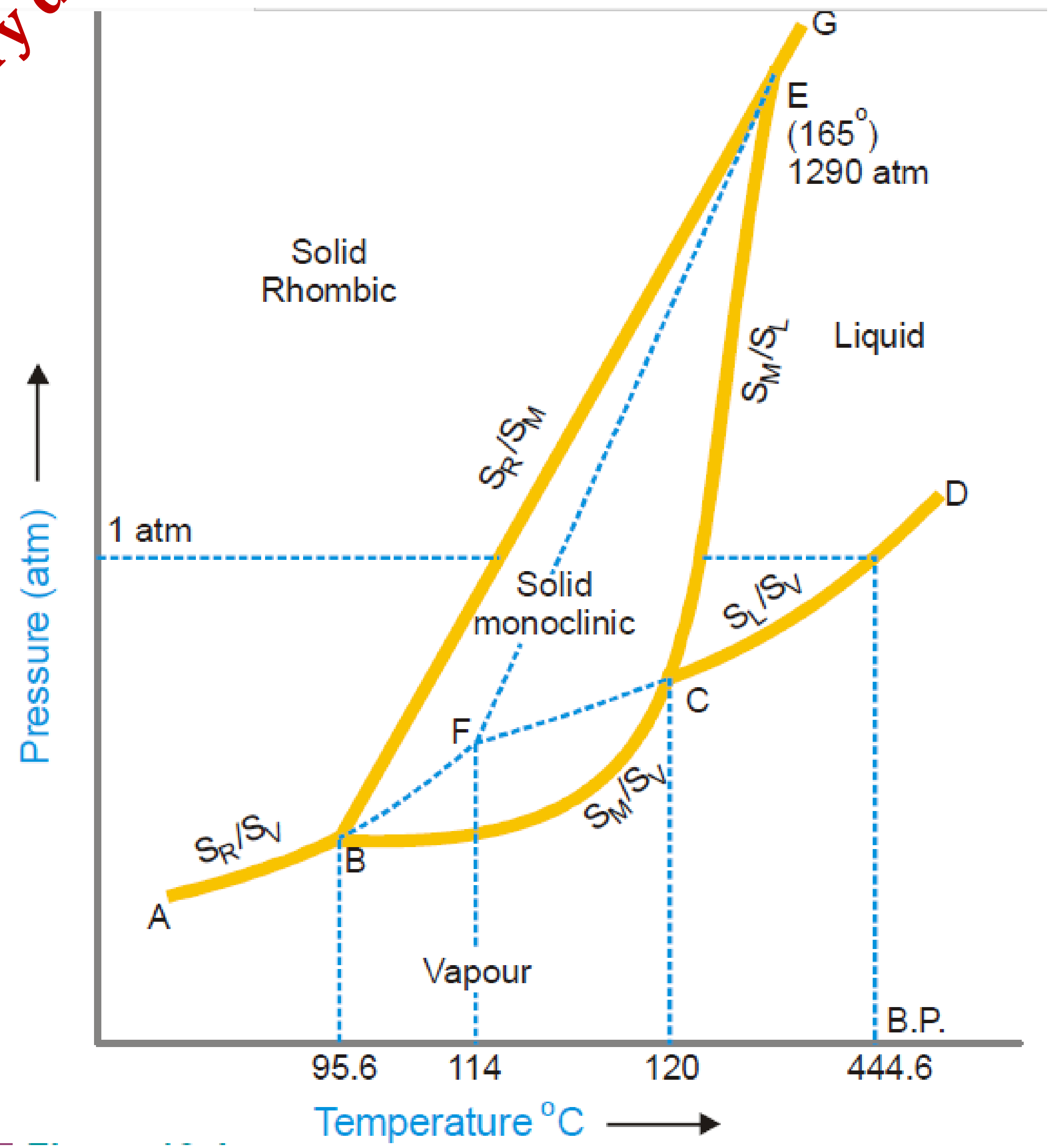

% AcOOH = 60

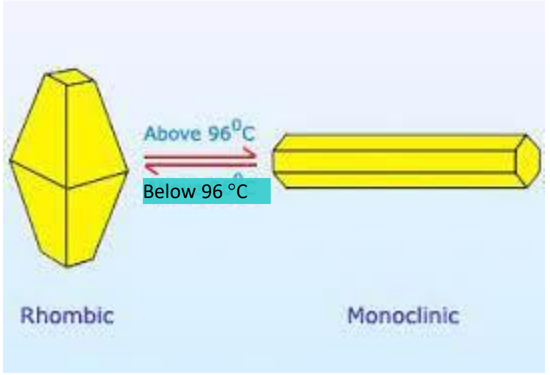
% BuOH = 30

% $H_2O$ = 10

Unary diagram

# Phase diagram of sulphur system

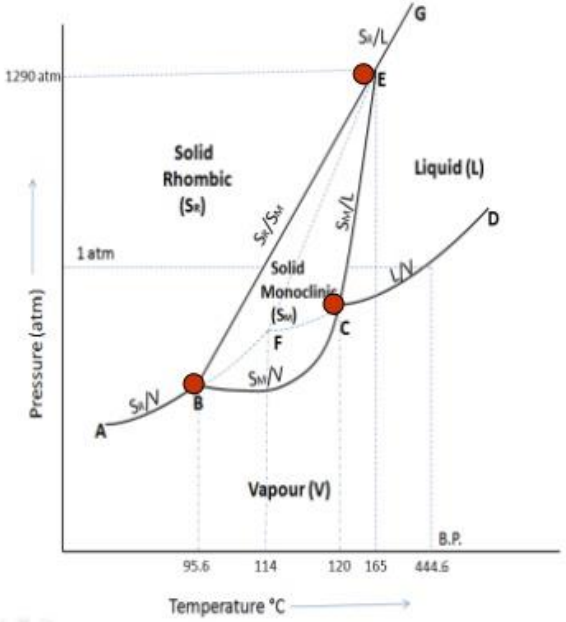


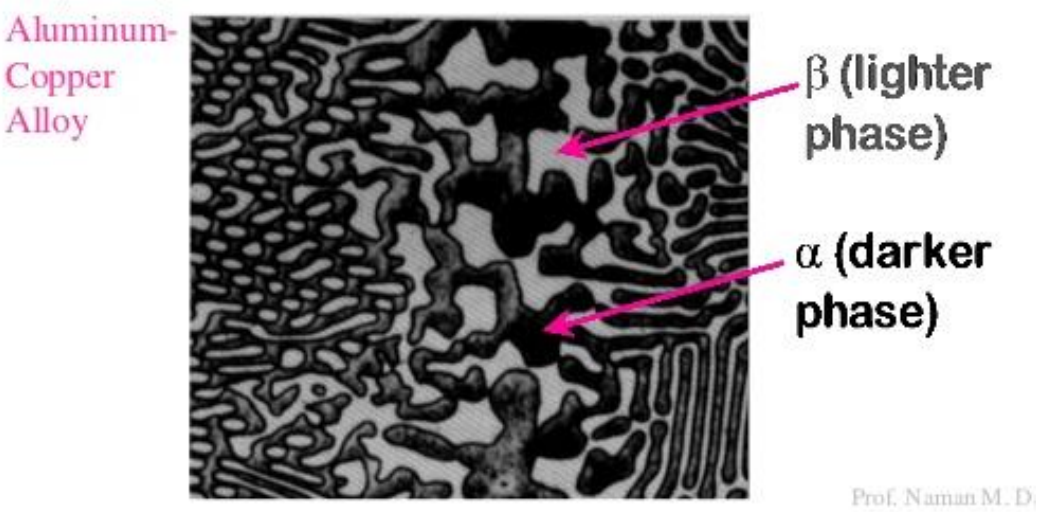

## Triple Points

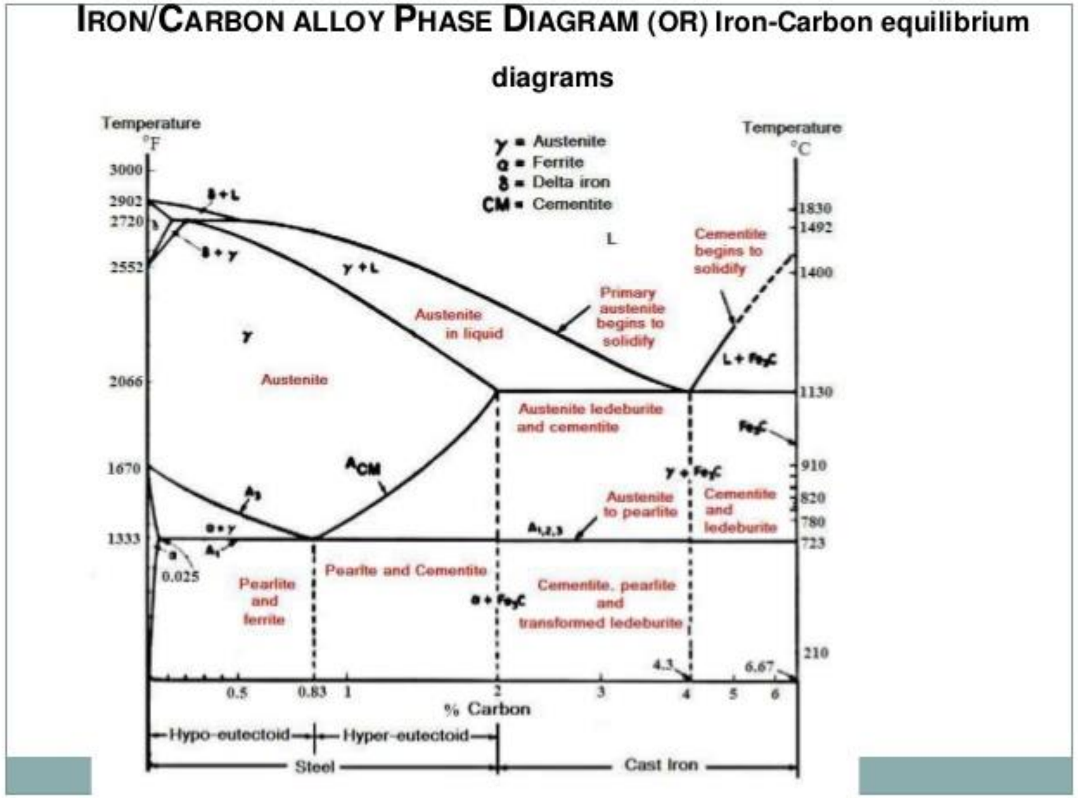
- Triple Point **B**
- Triple Point **C**
- Triple Point **E**

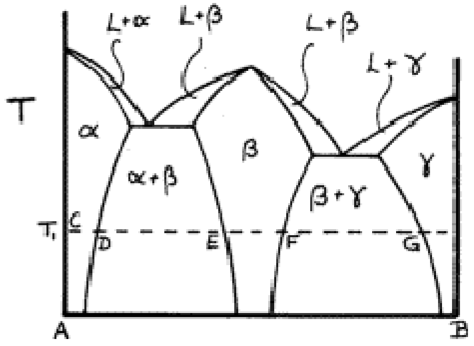
- At any Triple Point, phase rule becomes:
  F = 3-P = 3-3 = 0
  (nonvarient)



# Solid-solid system : Phase diagram of alloy



### (b) Water

Figure 4.9 is the phase diagram for water. The liquid–vapour boundary in the phase diagram summarizes how the vapour pressure of liquid water varies with temperature. It also summarizes how the boiling temperature varies with pressure: we simply read off the temperature at which the vapour pressure is equal to the prevailing atmospheric pressure. The solid–liquid boundary shows how the melting temperature varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes. The line has a steep negative slope (down from left to right) up to 2 kbar, which means that the melting temperature falls as the pressure is raised. The reason for this almost unique behaviour can be traced to the decrease in volume that occurs on melting: it is more favourable for the solid to transform into the liquid as the pressure is raised. The decrease in volume is a result of the very open structure of ice: as shown in Fig. 4.10, the water molecules are held apart, as well as together, by the hydrogen bonds between them but the hydrogen-bonded structure partially collapses on melting and the liquid is denser than the solid. Other consequences of its extensive hydrogen bonding are the anomalously high boiling point of water for a molecule of its molar mass and its high critical temperature and pressure.

Figure 4.9 shows that water has one liquid phase but many different solid phases other than ordinary ice ('ice I'). Some of these phases melt at high temperatures. Ice VII, for instance, melts at 100°C but exists only above 25 kbar. Two further phases, Ice XIII and XIV, were identified in 2006 at –160°C but have not yet been allocated regions in the phase diagram. Note that many more triple points occur in the diagram other than the one where vapour, liquid, and ice I coexist. Each one occurs at a definite pressure and temperature that cannot be changed. The solid phases of ice differ in the arrangement of the water molecules: under the influence of very high pressures, hydrogen bonds buckle and the $H_2O$ molecules adopt different arrangements. These polymorphs of ice may contribute to the advance of glaciers, for ice at the bottom of glaciers experiences very high pressures where it rests on jagged rocks.

**Fig. 4.8** The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied).

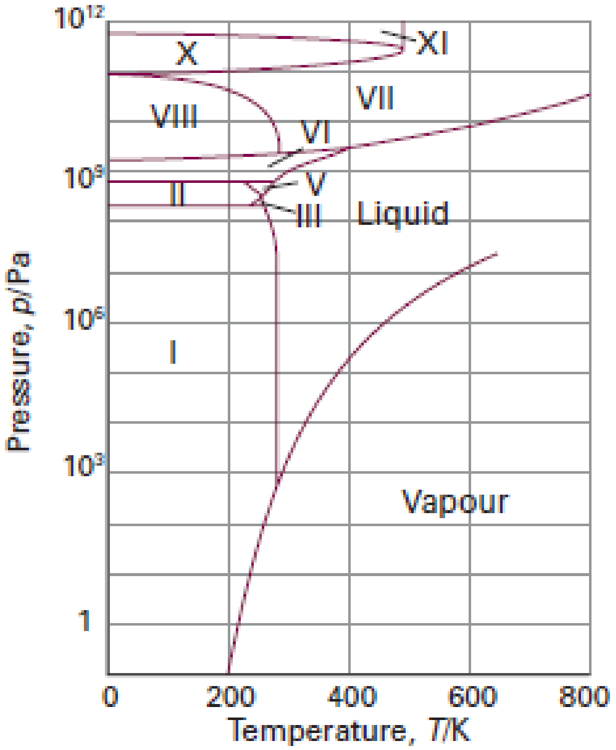
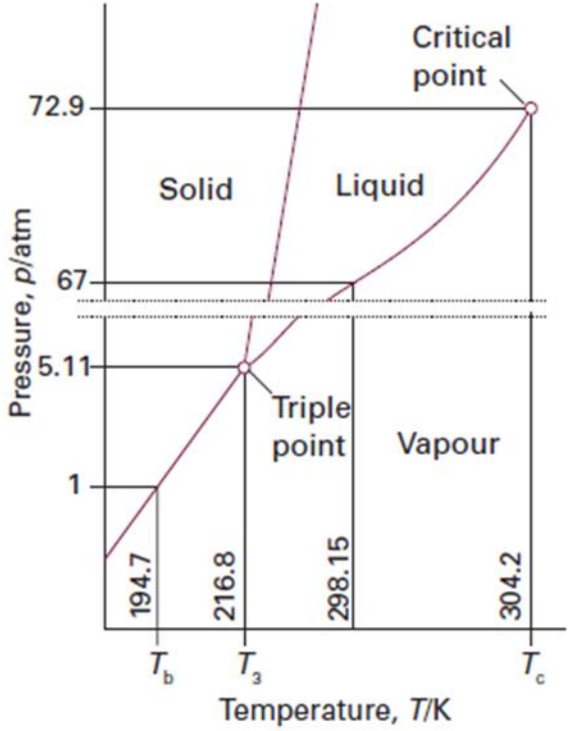



**Fig. 4.9** The experimental phase diagram for water showing the different solid phases.

### (a) Carbon dioxide

The phase diagram for carbon dioxide is shown in Fig. 4.8. The features to notice include the positive slope (up from left to right) of the solid–liquid boundary; the direction of this line is characteristic of most substances. This slope indicates that the melting temperature of solid carbon dioxide rises as the pressure is increased. Notice also that, as the triple point lies above 1 atm, the liquid cannot exist at normal atmospheric pressures whatever the temperature. As a result, the solid sublimes when left in the open (hence the name 'dry ice'). To obtain the liquid, it is necessary to exert a pressure of at least 5.11 atm. Cylinders of carbon dioxide generally contain the liquid or compressed gas; at 25°C that implies a vapour pressure of 67 atm if both gas and liquid are present in equilibrium. When the gas squirts through the throttle it cools by the Joule–Thomson effect, so, when it emerges into a region where the pressure is only 1 atm, it condenses into a finely divided snow-like solid. That carbon dioxide gas cannot be liquefied except by applying high pressure reflects the weakness of the intermolecular forces between the nonpolar carbon dioxide molecules (Section 17.5).

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