University of Science
Department of Materials science

Chapter 7

Phase Equilibrium in a One-Component System

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Outline

1. Definition of a Phase

2. Phase Equilibrium

3. Phase Diagram for One-Component System

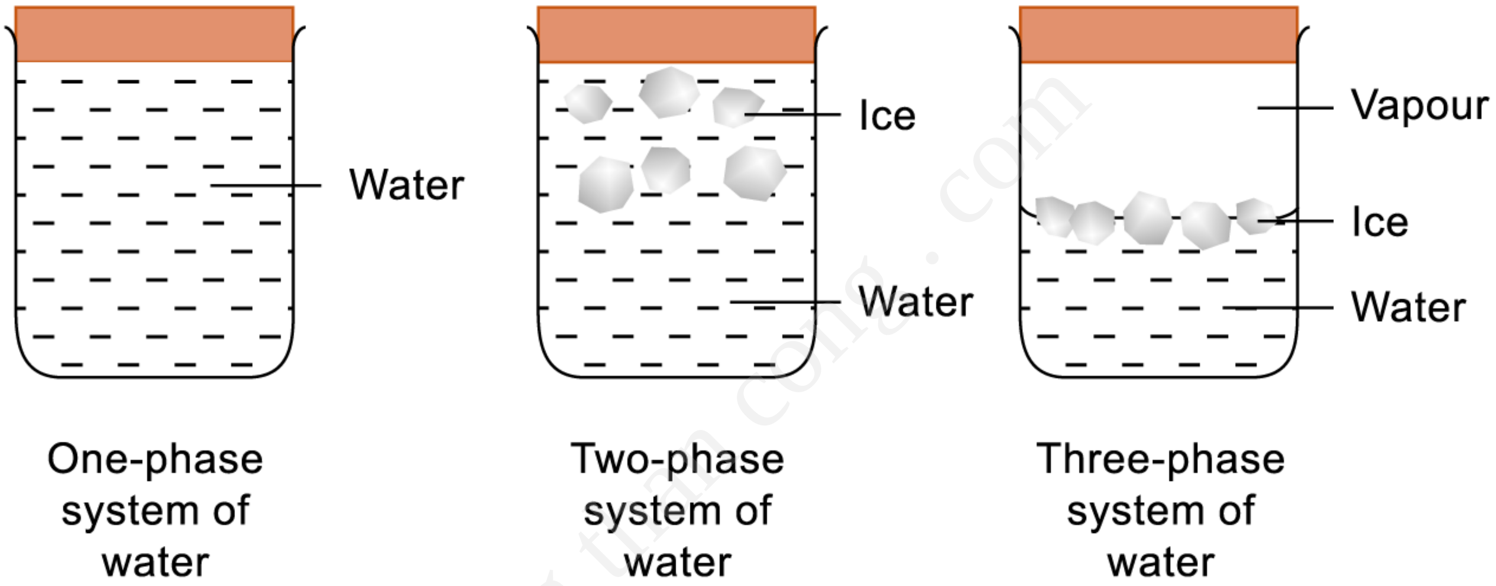
1. Definition of a Phase

Definition of a phase

Phase

- Any part of a system which is physically separated from other parts of the system by a *distinct boundary*.
- A phase can be a solid, liquid, vapour (gas) or aqueous solution which is *uniform in both chemical constitution and physical state*.

1. Definition of a Phase



Heterogeneous system ---- system with more than one phase

Homogeneous system ---- system consists of one phase only

1. Definition of a Phase

The phases of various systems

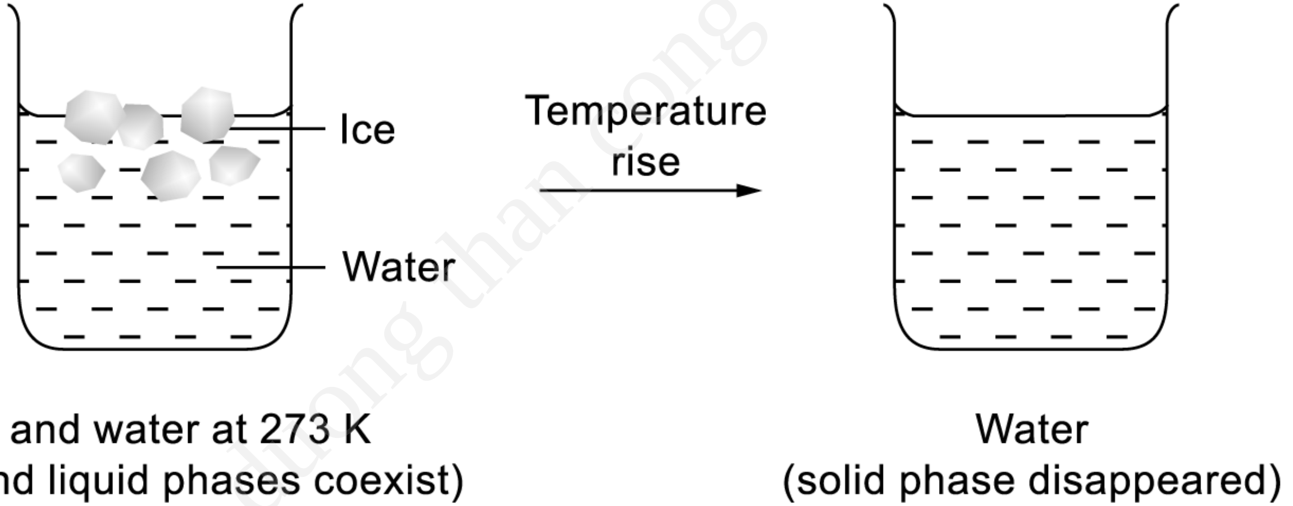
Type of system	System	Example	Number of phases
Homogeneous	Mixture of gases	Air (mixture of N_2, O_2, CO_2…)	1 gaseous phase
Homogeneous	Mixture of two miscible liquids	Ethanol and water	1 liquid phase
Homogeneous	Mixture of two immiscible liquids	Salt and sand	2 solid phases
Homogeneous	Mixture of two solids	Ice and water	1 solid phase and 1 liquid phase

1. Definition of a Phase

The phases of various systems

Heterogeneous	Mixture of a solid and a liquid	Ice, water and vapour	1 solid phase, 1 liquid phase and 1 gaseous phase
Heterogeneous	Mixture of a solid, a liquid and a gas	Ice, water and vapour	1 solid phase, 1 liquid phase and 1 gaseous phase
Heterogeneous	Mixture of two solids and a gas	$CaCO_3$, CaO and CO_2	2 solid phases and 1 gaseous phase

Phase Equilibrium

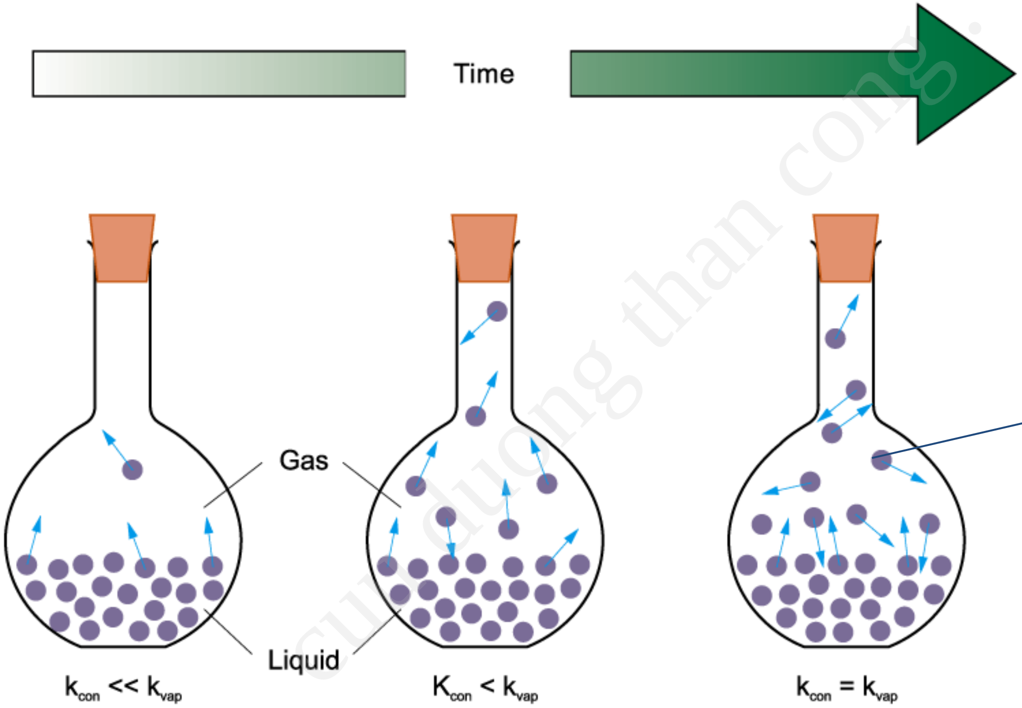


A *phase equilibrium* is a balance between phases, that is the coexistence of two or more phases in a state of *dynamic equilibrium*.

A component is a *chemical species* which may be used to specify the composition of a system.

Evaporation and Condensation

At a fixed temperature



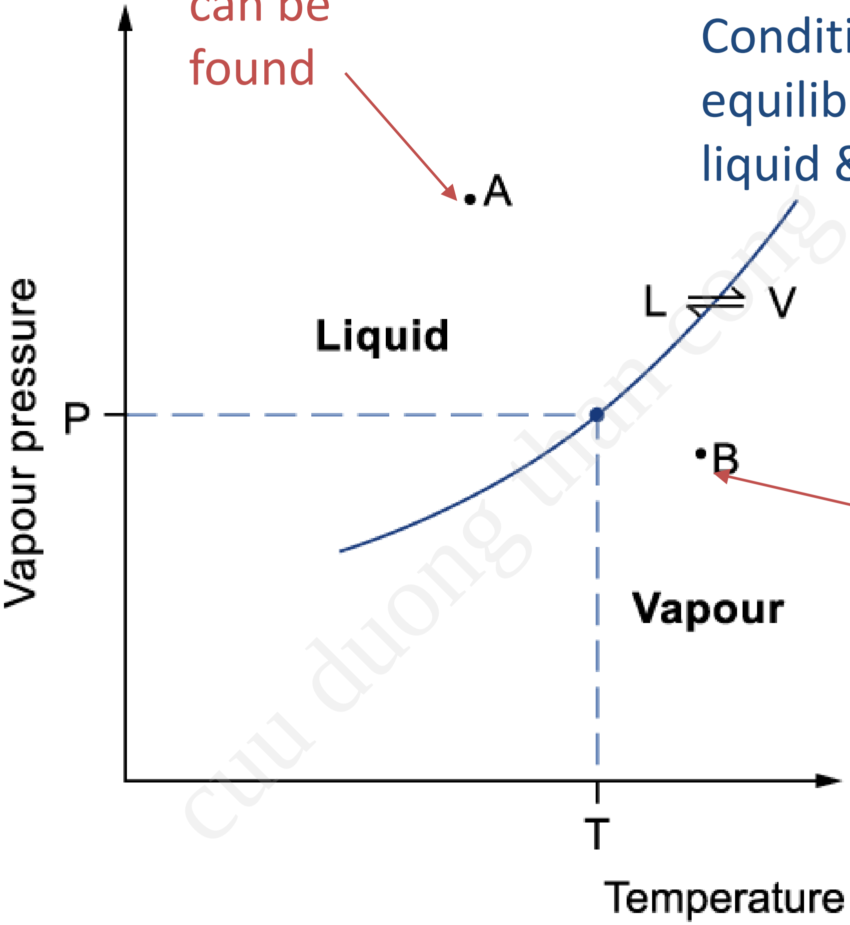
Saturated vapour pressure

(a dynamic equilibrium)

A phase equilibrium

2. Phase Equilibrium

From expt: s.v.p. ↑ with temperature.



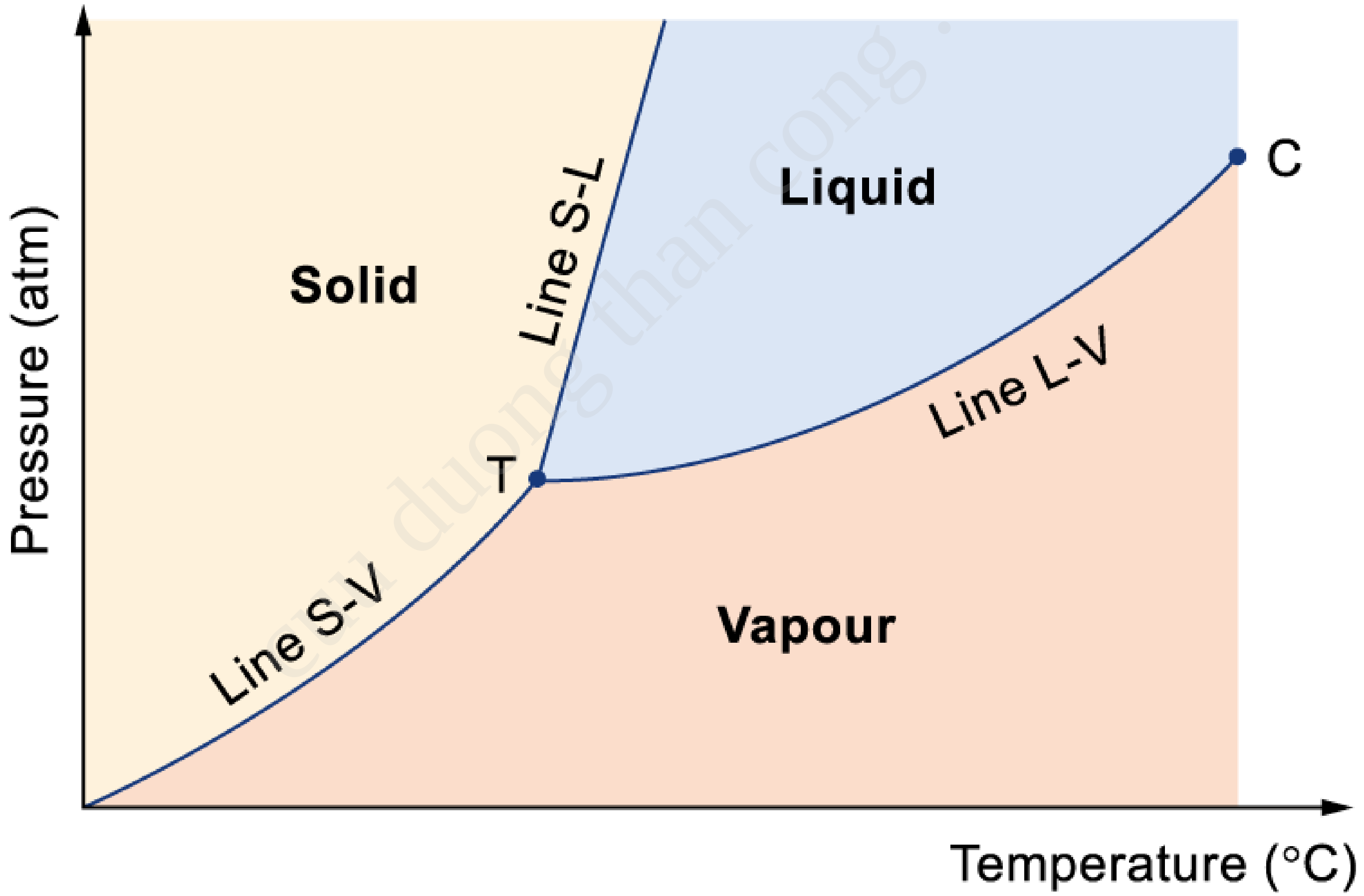
Only liquid can be found

Conditions at which phase equilibria occur between liquid & vapour.

Only vapour can be found

A phase diagram

One Component System - General



The general features of a phase diagram

Region/Line/ Point	Name	Dynamic equilibrium
Region	Solid	Only solid phase exists.
	Liquid	Only liquid phase exists.
	Vapour	Only vapour phase exists
Line	S-L (fusion curve)	Solid and liquid phases are in equilibrium.
	L-V (vaporization curve)	Liquid and vapour phases are in equilibrium.
	S-V (sublimation curve)	Solid, liquid and vapour phases are in equilibrium.
Point	T (triplet point)	Solid, liquid and vapour phases in equilibrium.
	C (critical point)	Beyond this point, the vapour cannot be changed into liquid by altering the pressure alone.

THE VARIATION OF GIBBS FREE ENERGY WITH TEMPERATURE AT CONSTANT PRESSURE

$$H_2O_{(solid)} \rightarrow H_2O_{(liquid)} \text{ at 1 atm and 273 K}$$

$$\Delta G = G_{H_2O_{(l)}} - G_{H_2O_{(s)}} = 0$$

Thus, **at the state of equilibrium between ice and water**,

$$G_{H_2O_{(l)}} = G_{H_2O_{(s)}} \qquad (7.1)$$

where $G_{H_2O_{(s)}}$ is the molar Gibbs free energy of H_2O in the solid (ice) phase, and $G_{H_2O_{(l)}}$ is the molar Gibbs free energy of H_2O in the liquid (water) phase. For the system of ice+water containing n moles of H_2O, $n_{H_2O_{(s)}}$ which are in the ice phase and $n_{H_2O_{(l)}}$ of which are in the water phase, the Gibbs free energy of the system, G', is

$$G' = n_{H_2O_{(s)}} G_{H_2O_{(s)}} + n_{H_2O_{(l)}} G_{H_2O_{(l)}} \qquad (7.2)$$

where $G_{H20\ (l)}$ is the molar Gibbs free energy of H2O in the solid (ice) phase, and $G_{H20\ (s)}$ is the molar Gibbs free energy of H2O in the liquid (water) phase.

For the system of ice + water containing *n* moles of H_2O

$$G' = n_{H_2O_{(s)}} G_{H_2O_{(s)}} + n_{H_2O_{(l)}} G_{H_2O_{(l)}} \tag{7.2}$$

The chemical potential of a species in a particular state equals the molar Gibbs free energy of the species in the particular state.

$$\left(\frac{\partial G'}{\partial n_i}\right)_{T,P} = \mu_i$$

In a one-component system, the chemical potential of the component equals the increase in the value of *G'* which occurs when 1 mole of the component is added to the system at constant *T* and *P*. That is, if the component is the species *i*,

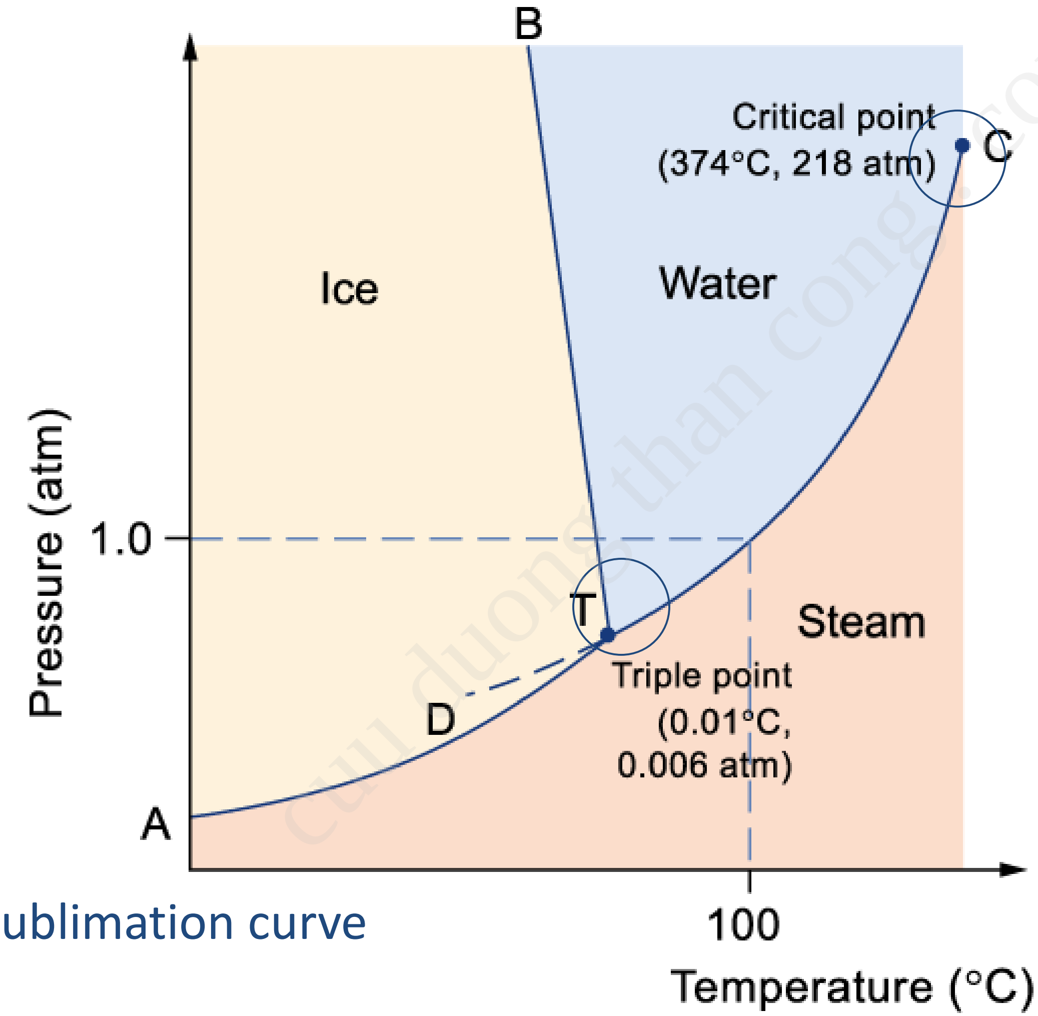
$$\Delta G' = \mu_i$$

and as the increase in the value of *G'* for the one-component system is simply the molar Gibbs free energy of *i*, then

$$G_i = \mu_i$$

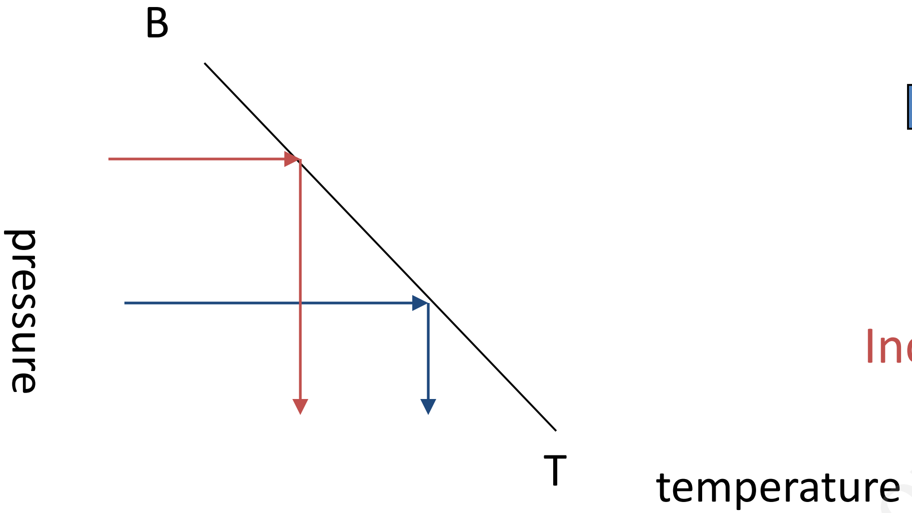
Phase Diagram of Water

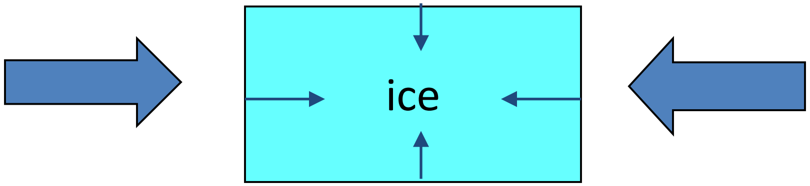
TB= fusion curve (-ve slope for water) - unusual



TC= vaporization curve

TA= sublimation curve

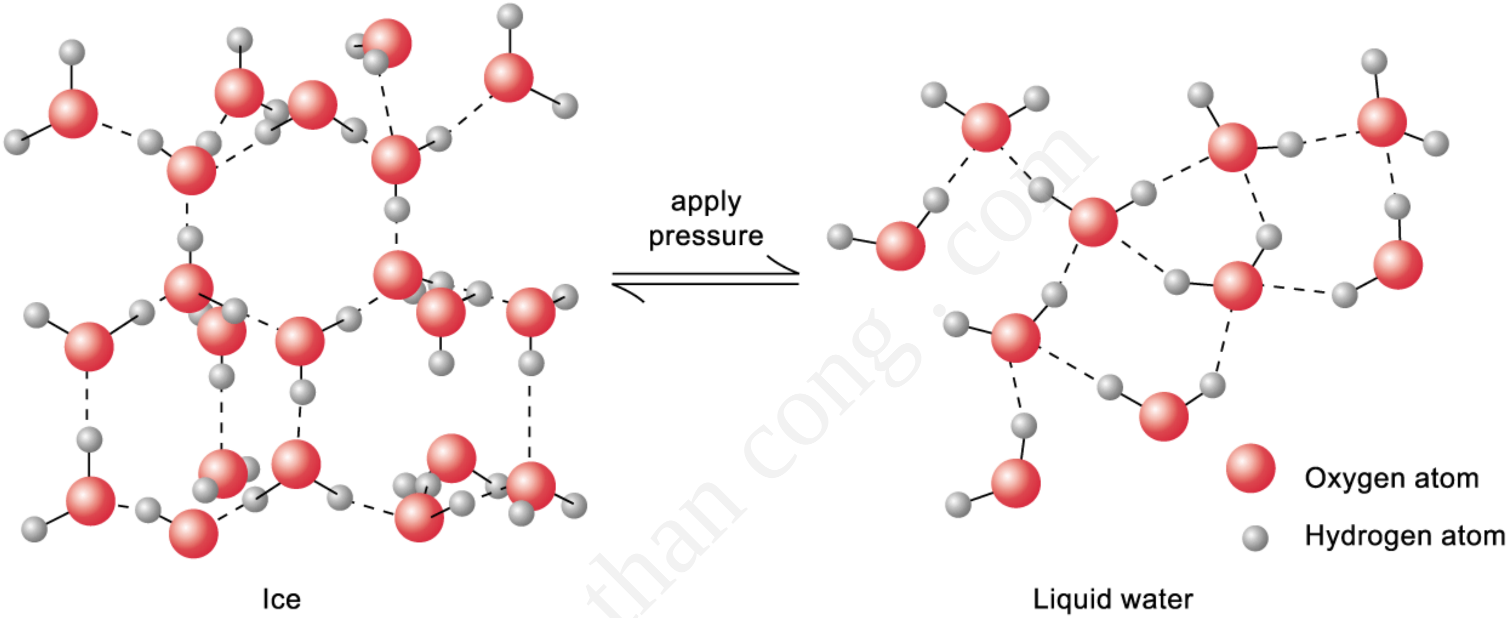




Ice contracts when melted.

Increase in pressure enhances melting.

An increase in pressure lowers the m.p. of water.

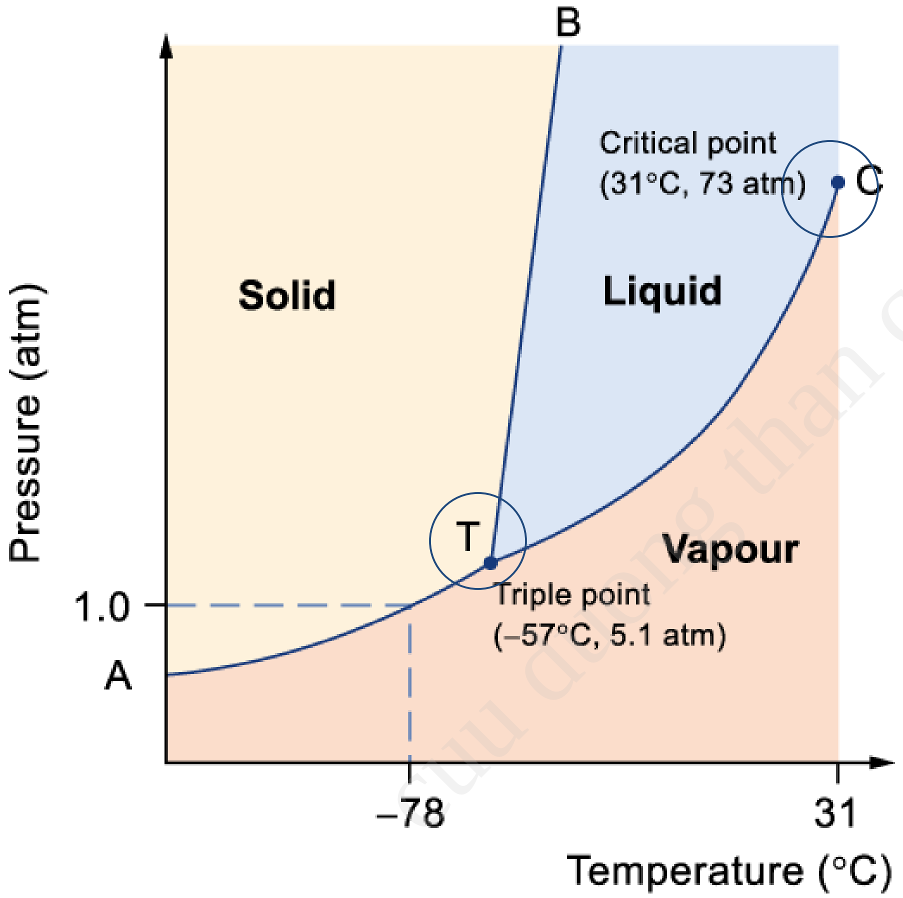


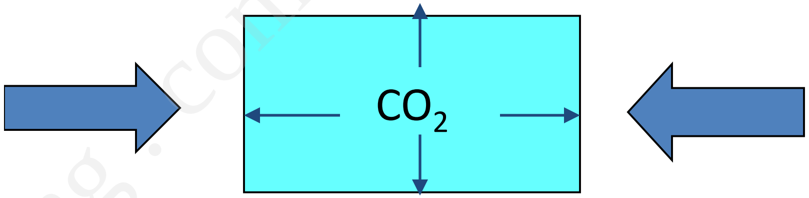
Contraction in volume

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

By Le Chatelier's principle, the effect of increasing the pressure will favour a reduction in volume, causing the equilibrium to be shifted to the right.

Phase Diagram of Carbon Dioxide





Solid CO_2 expands when melted.

crease in pressure inhibits melting.

TC= vaporization curve

TB= fusion curve (+ve slope for CO_2) - usual

TA= sublimation curve

T above 1 atm $\Rightarrow$ solid CO_2 sublimes when left in a warm atmosphere

GIBBS FREE ENERGY AS A FUNCTION OF TEMPERATURE AND PRESSURE

$$G_{(l)} = G_{(s)}$$

or, for any infinitesimal change in T and P,

$$dG_{(l)} = dG_{(s)}$$

From Eq. (5.12)

$$dG_{(l)} = -S_{(l)}dT + V_{(l)}dP$$

and

$$dG_{(s)} = -S_{(s)}dT + V_{(s)}dP$$

Thus, for equilibrium to be maintained between the two phases,

$$-S_{(l)}dT + V_{(l)}dP = -S_{(s)}dT + V_{(s)}dP$$

or

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S_{(s)} - S_{(l)}}{V_{(s)} - V_{(l)}} = \frac{\Delta S_{(l\to s)}}{\Delta V_{(l\to s)}}$$

At equilibrium $\Delta G=0$, and hence $\Delta H=T\Delta S$, substitution of which into the above equation gives

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T\Delta V}$$

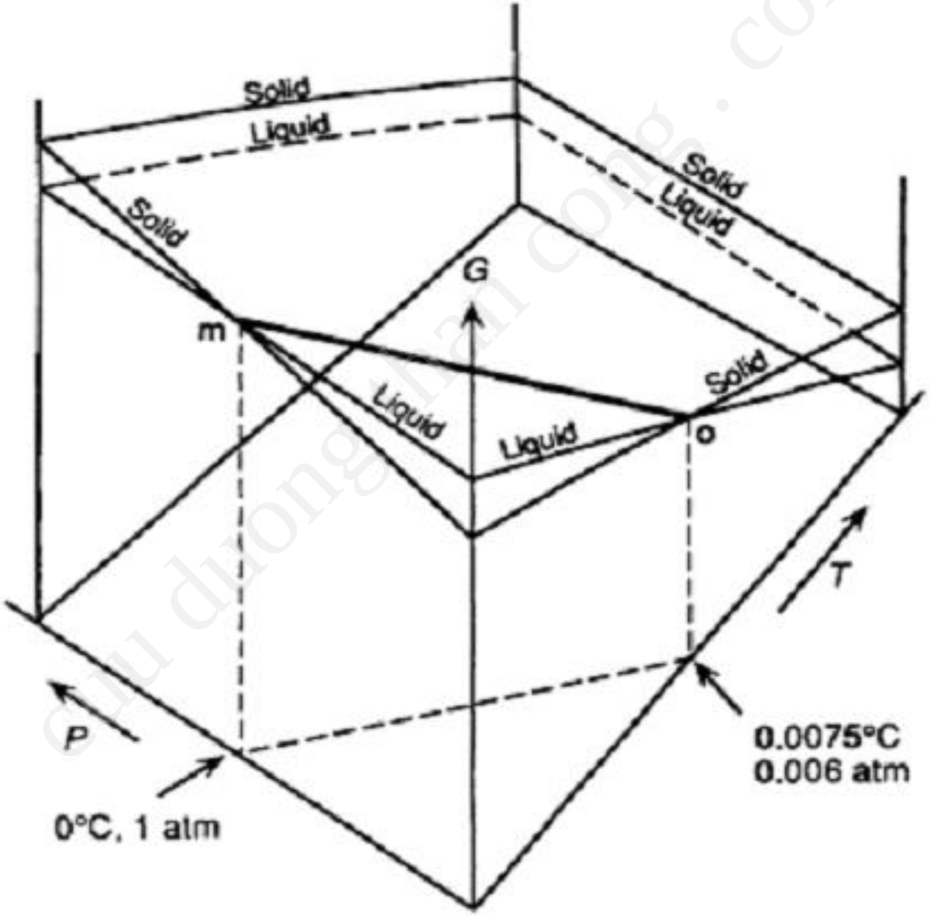


Figure 7.8 Schematic representation of the equilibrium surfaces of the solid and liquid phases of water in G-T-P space.

EQUILIBRIUM BETWEEN THE VAPOR PHASE AND A CONDENSED PHASE

$$\Delta V = V_{\text{vapor}} - V_{\text{condensed phase}}$$

and as V_{vapor} is very much larger than $V_{\text{condensed phase}}$, then, with the introduction of an insignificant error,

$$\Delta V = V_{\text{vapor}}$$

Thus, for condensed phase-vapor equilibria, Eq. (7.5) can be written as

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{\Delta H}{TV_{(v)}}$$

in which $V_{(v)}$ is the molar volume of the vapor. If it is further assumed that the vapor in equilibrium with the condensed phase behaves ideally, i.e., $PV=RT$, then

$$\left(\frac{dP}{dT}\right)_{\text{eq}} = \frac{P\Delta H}{RT^2}$$

rearrangement of which gives

$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT$$

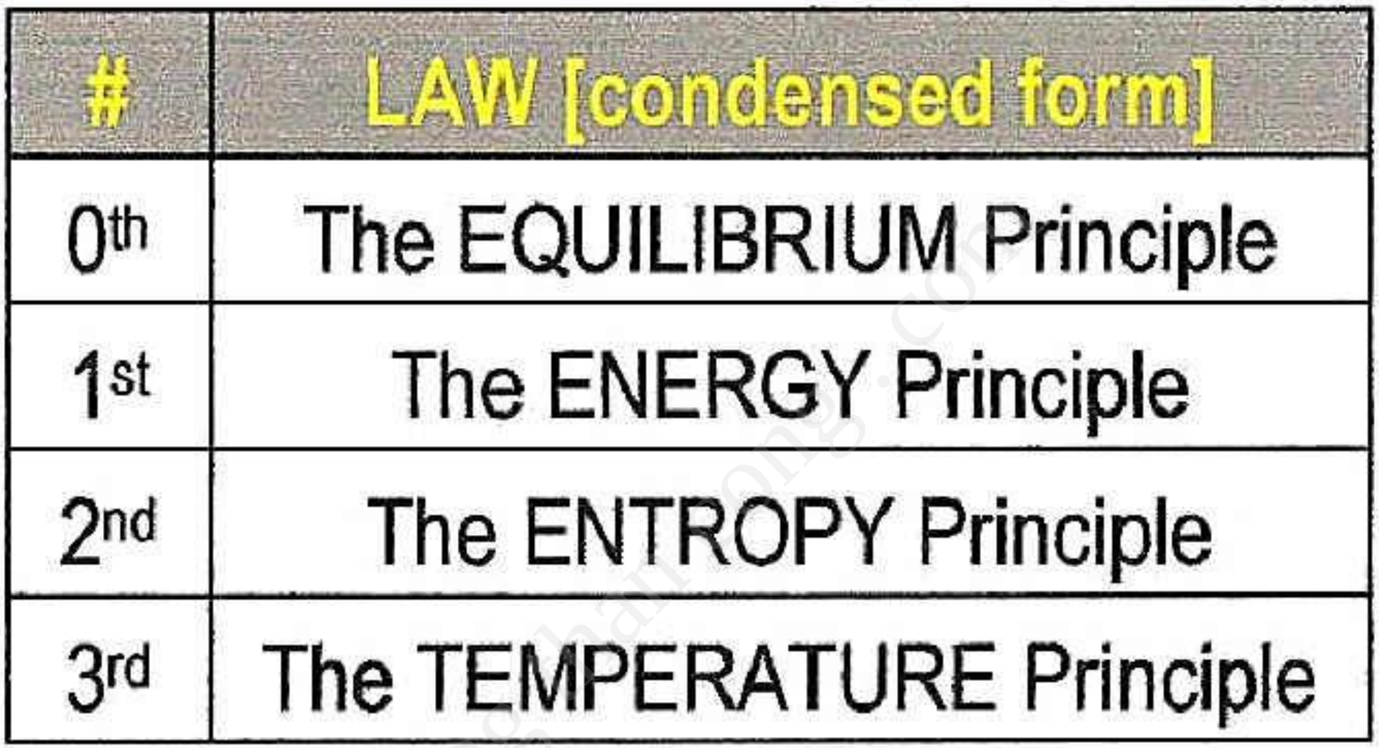
or

$$d \ln P = \frac{\Delta H}{RT^2} dT \tag{7.6}$$

Eq. (7.6) is known as the Clausius-Clapeyron equation.

If ΔH is independent of temperature, i.e., if C_p(vapor)=C_p(condensed phase), integration of Eq. (7.6) gives

$$\ln P = -\frac{\Delta H}{RT} + \text{constant} \tag{7.7}$$



#	LAW [condensed form]
0th	The EQUILIBRIUM Principle
1st	The ENERGY Principle
2nd	The ENTROPY Principle
3rd	The TEMPERATURE Principle

The END