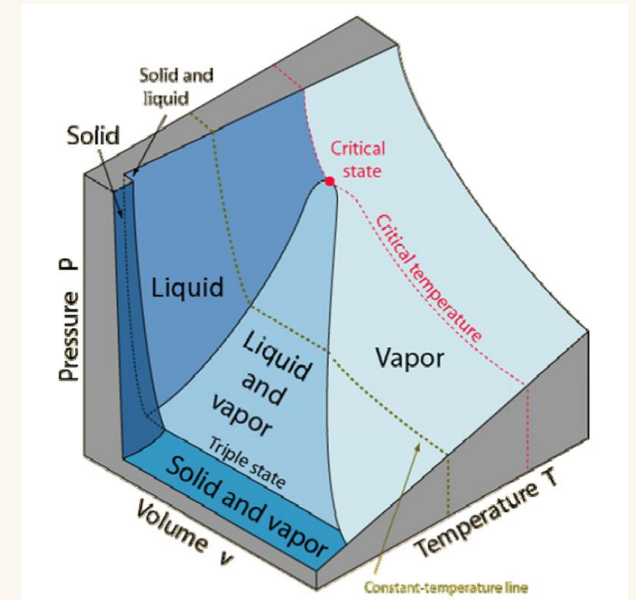# PHAS1000 – THERMAL PHYSICS

Lecture 9

Phase Changes

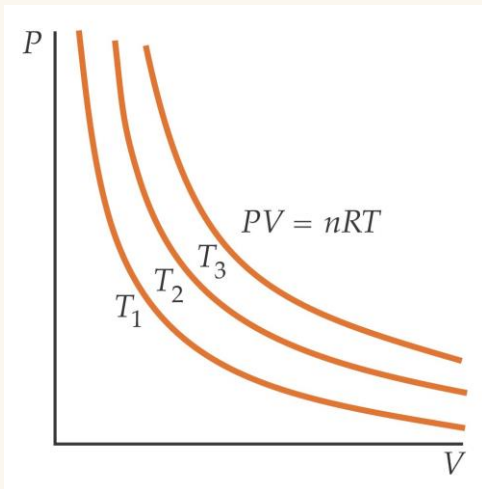# Overview

This lecture covers:
- ➤ Real Gases
- ➤ Van der Waals equation
- ➤ Phase diagrams
- ➤ Saturated vapour pressure (svp)
- ➤ Dew point

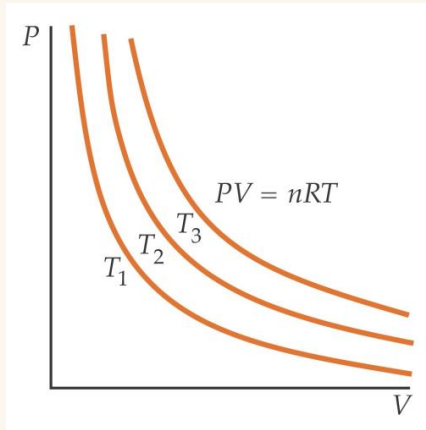# What is a real gas?

Ideal gases

Which assumptions of kinetic theory do not hold for real gases?

- Gas contains many molecules
- Molecules well separated
- Direction of molecules is random
- Molecules exert no force on each other
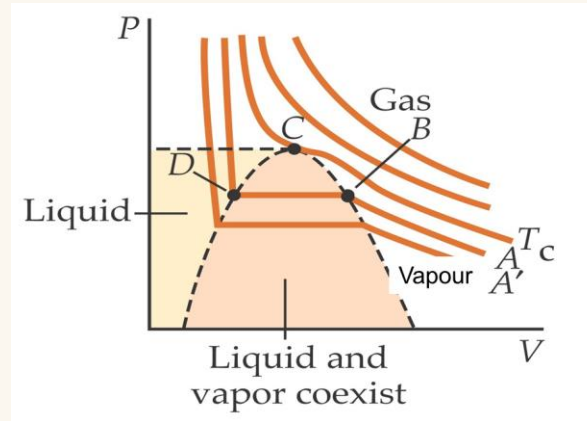- Elastic collisions

Van der Waals equation

Ideal gases

$$PV = nRT$$

Real gases

Van der Waals equation of state

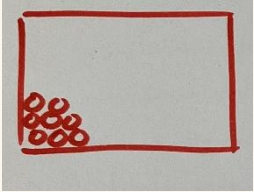$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT$$

P is higher than measured

V is lower than measured
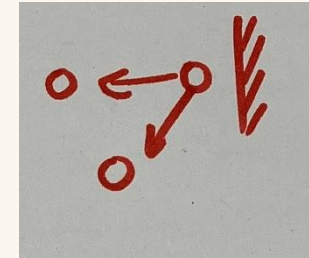
Meaning of constants a and b

b = actual volume of one mole of gas molecules.

Gas molecules have finite size, so free volume available to each molecule is reduced.

$\dfrac{an^2}{V^2}$ due to the attractions between the molecules.

As a molecule approaches the wall it is pulled back by surrounding molecules with a force proportional to density $\dfrac{n}{V}$

But number of molecules that hit the wall per second is also proportional to density. Thus attractive force goes as $\left(\dfrac{n}{V}\right)^2$

a depends on the gas, and is small for inert gases, e.g. Helium, Neon and Argon.

Question 1

Calculate the density of liquid nitrogen if b = 39.1mL.mol^{-1} for nitrogen molecules.

$$\rho = \frac{mass}{volume} = \frac{Molar\ Mass}{Molar\ Volume} = \frac{M}{b} = \frac{28 \times 10^{-3}}{39.1 \times 10^{-6}} = 716\ kg\,m^{-3}$$

# Johannes Diderik Van der Waals

❏ Born in Leyden, Holland

❏ PhD on 'continuity of the gas and liquid phase' to interpret experiments by Andrews

❏ Discovered that it is important to take account of size of molecules and their interactions in a real gas

❏ These intermolecular interactions now known as Van der Waals interactions

❏ James Clerk Maxwell recognised that he would soon be a famous scientist

❏ Received honorary doctorate from Cambridge University

❏ Received Nobel prize in 1910

1837-1923

Vapour
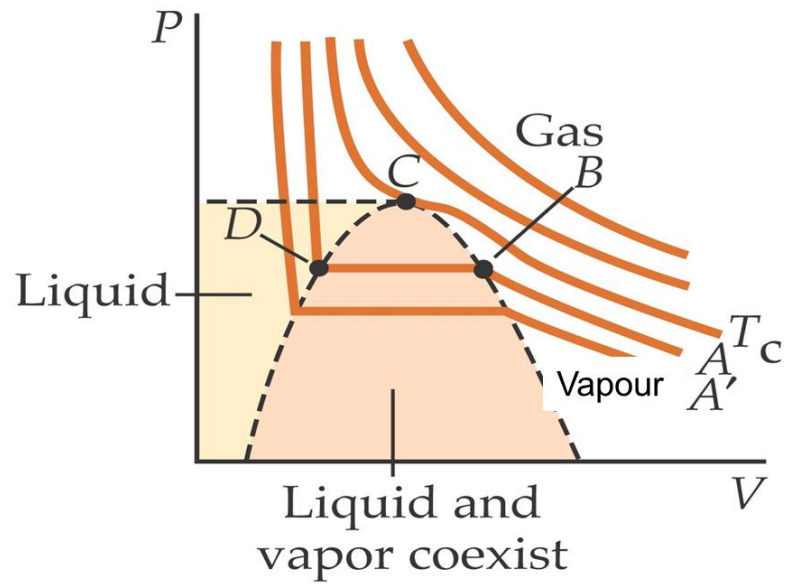
What is a vapour?

What is a vapour?

Critical Temperature
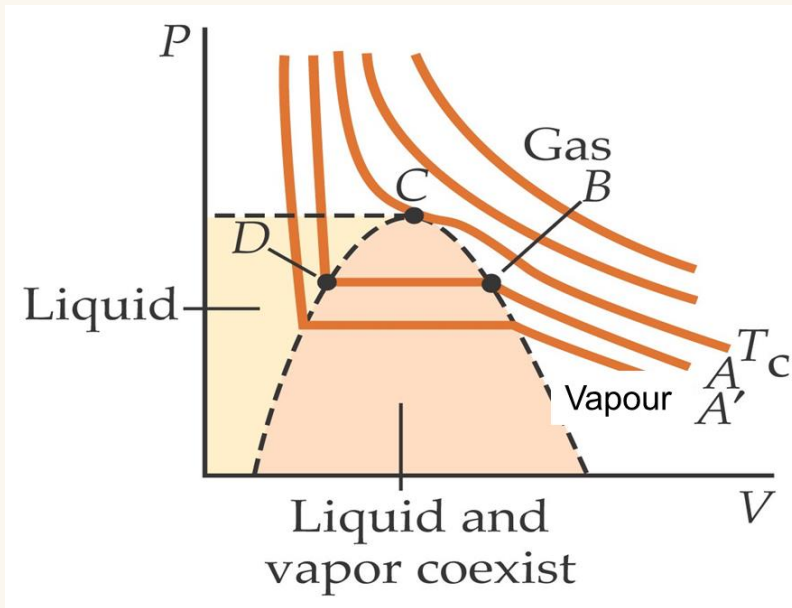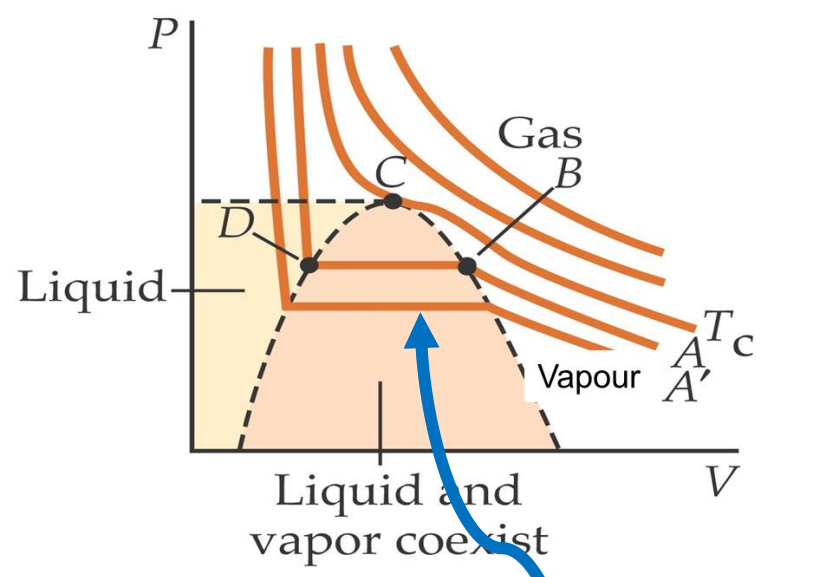
At temperatures below the critical isotherm (T_C) the gas can be liquified at high pressure, and hence is termed a vapour

At temperatures above the critical isotherm the gas cannot be liquified, however high the pressure

For water T_C = 647K = 374°C

Vapour Pressure
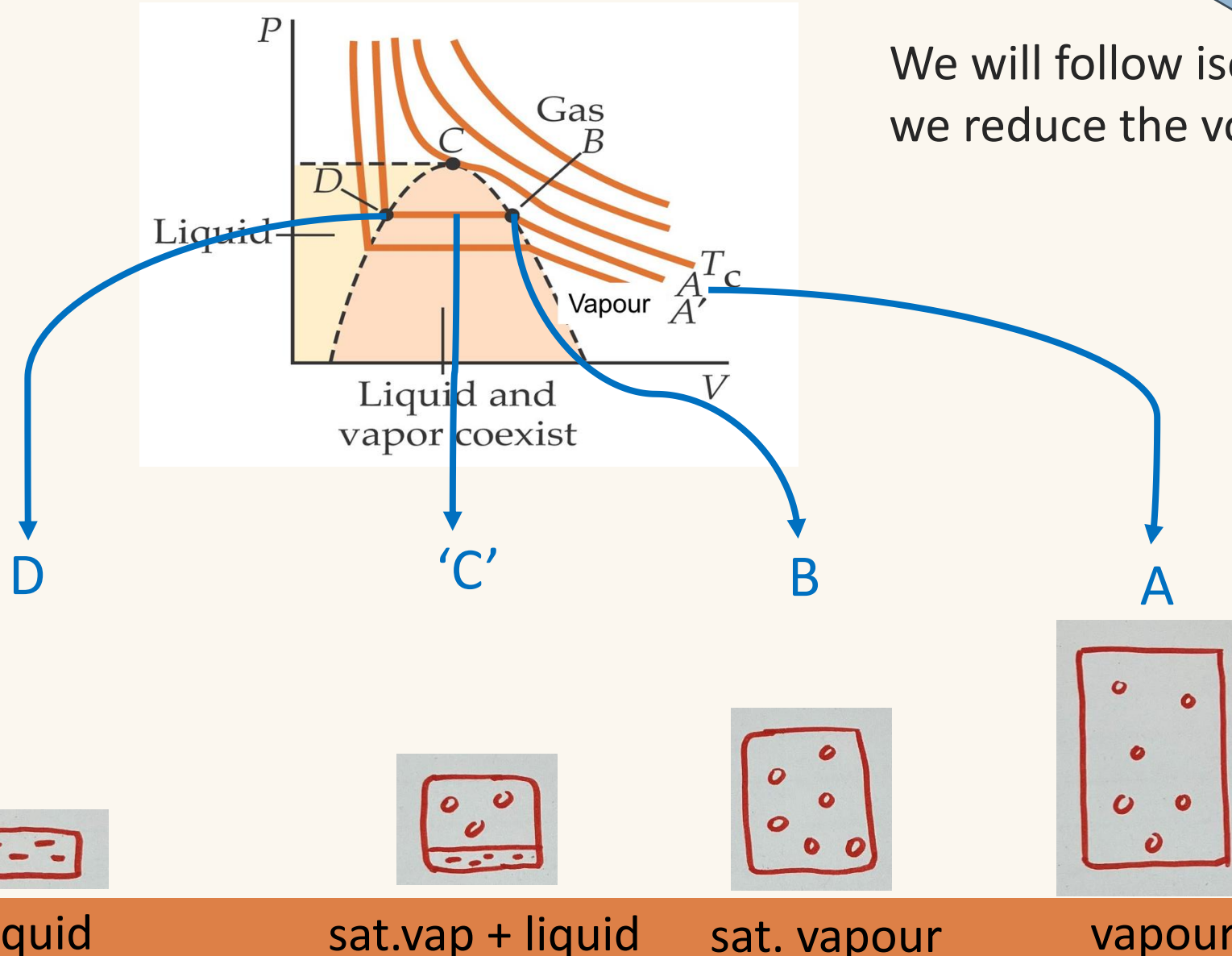

A **saturated vapour** is one in equilibrium with its liquid. (Horizontal lines on graph).

Compressing a vapour

We will follow isotherm A as we reduce the volume.......

D   'C'   B   A

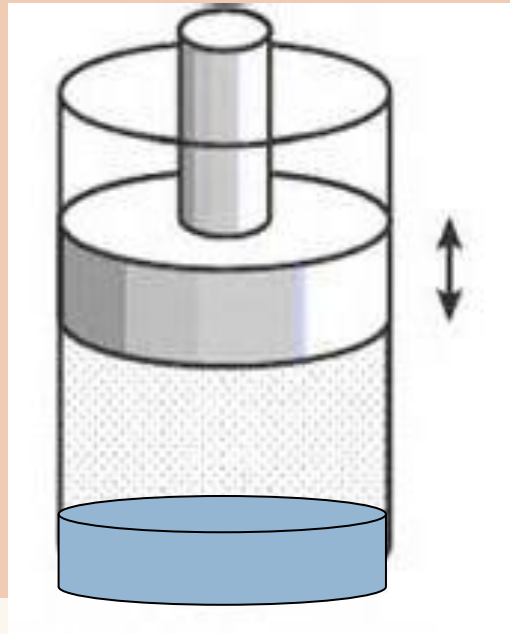liquid   sat.vap + liquid   sat. vapour   vapour

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Question 2

A closed cylinder contains liquid water and water vapour in equilibrium at 20°C. The piston is slowly pushed down until the volume inside is halved, but still at 20°C. What happens to the water vapour pressure?

A   It doubles.

B   It more than doubles.

C   It remains the same.

D   It decreases.

A   It doubles

##.##%

B   It more than doubles

##.##%

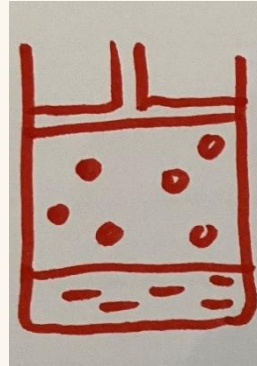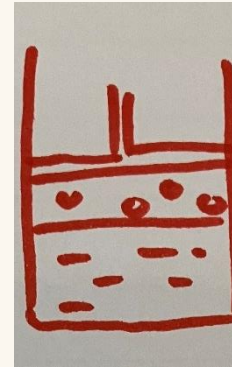C   It remains the same

##.##%

D   It decreases

##.##%

Answer Q2

A closed cylinder contains liquid water and water vapour in equilibrium at 20°C.
The piston is slowly pushed down until the volume inside is halved, but still at 20°C. What happens to the water vapour pressure?

A It doubles.

B It more than doubles.

C It remains the same.

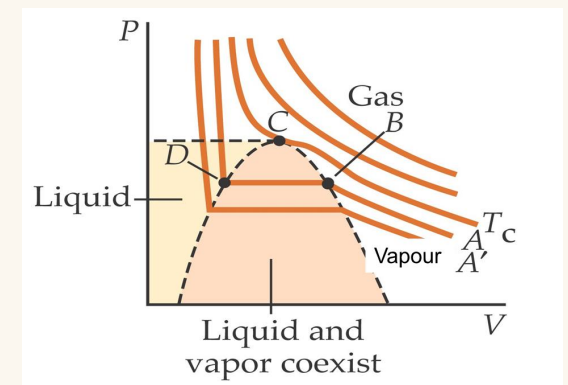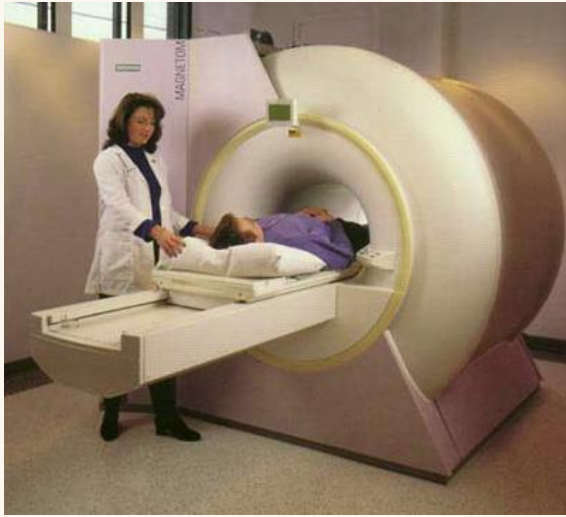D It decreases.

ANS C

before   after

Less vapour, but still at SVP

More liquid

'Liquid and vapour in equilibrium' implies vapour is at SVP. (horizontal part of curve).
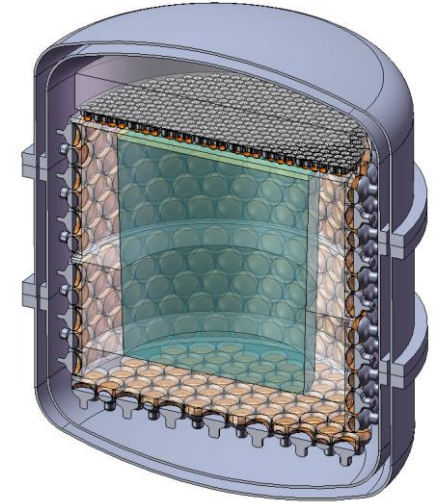
# Uses of cryogens – gases liquified at low temperature

Liquid helium (4K): used to cool superconducting magnets in MRI.

Liquid argon (87K): detector used to look for WIMP particles (dark matter) since they should produce light as they interact with argon nucleus.
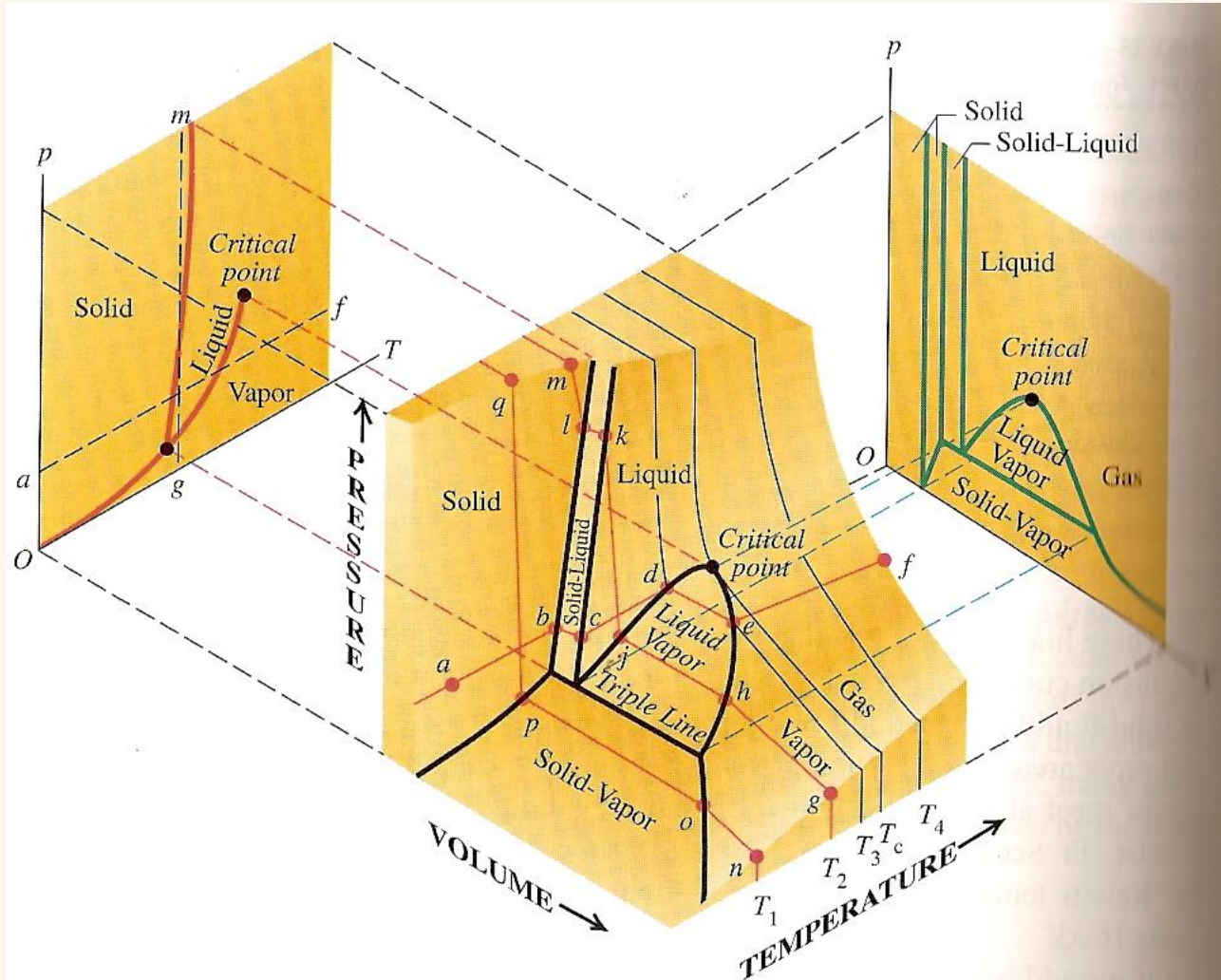

Liquid methane (112K): Lakes on Titan (Saturn moon) are liquid methane. Observed by the Cassini-Huygens space probe
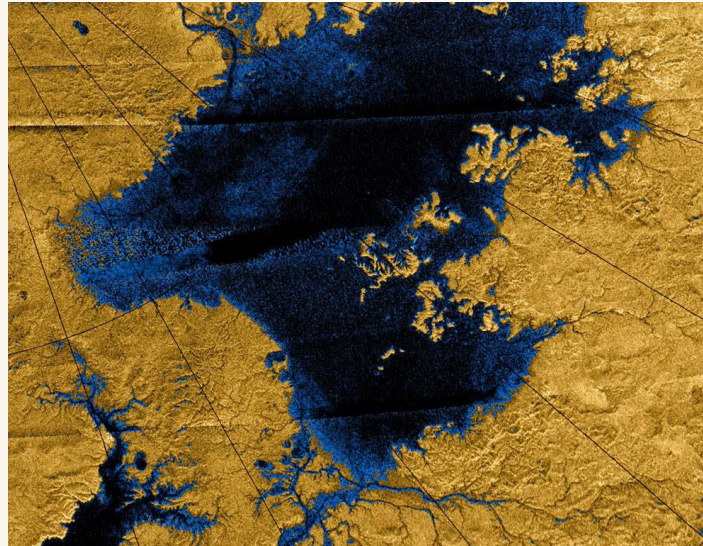
Liquid nitrogen (77K): Storage of biological samples (blood, sperm, eggs) Cryotherapy: removal of warts etc Transportation of food
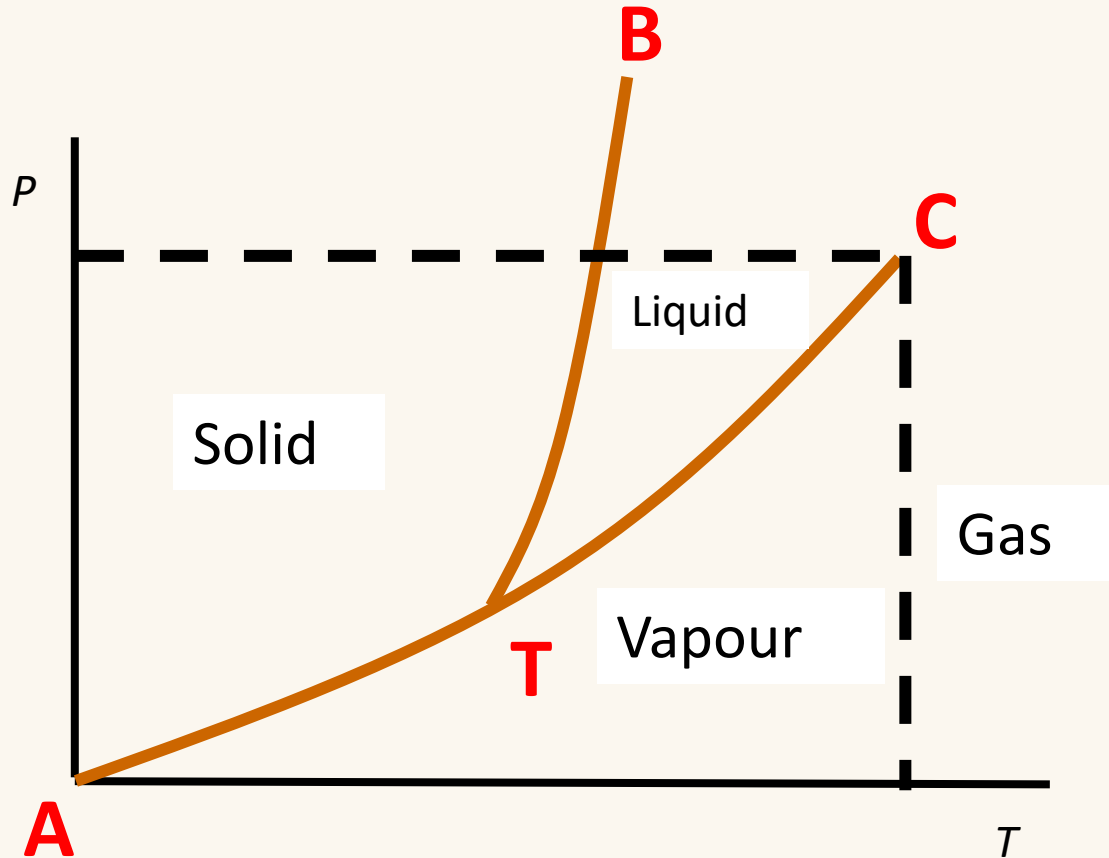
PVT space

This video (from Open University) gives a tour of this 3D space)

critical point and triple point 2/13/2015 (leeds.ac.uk)

Phase Diagrams

Phase diagram for most substances
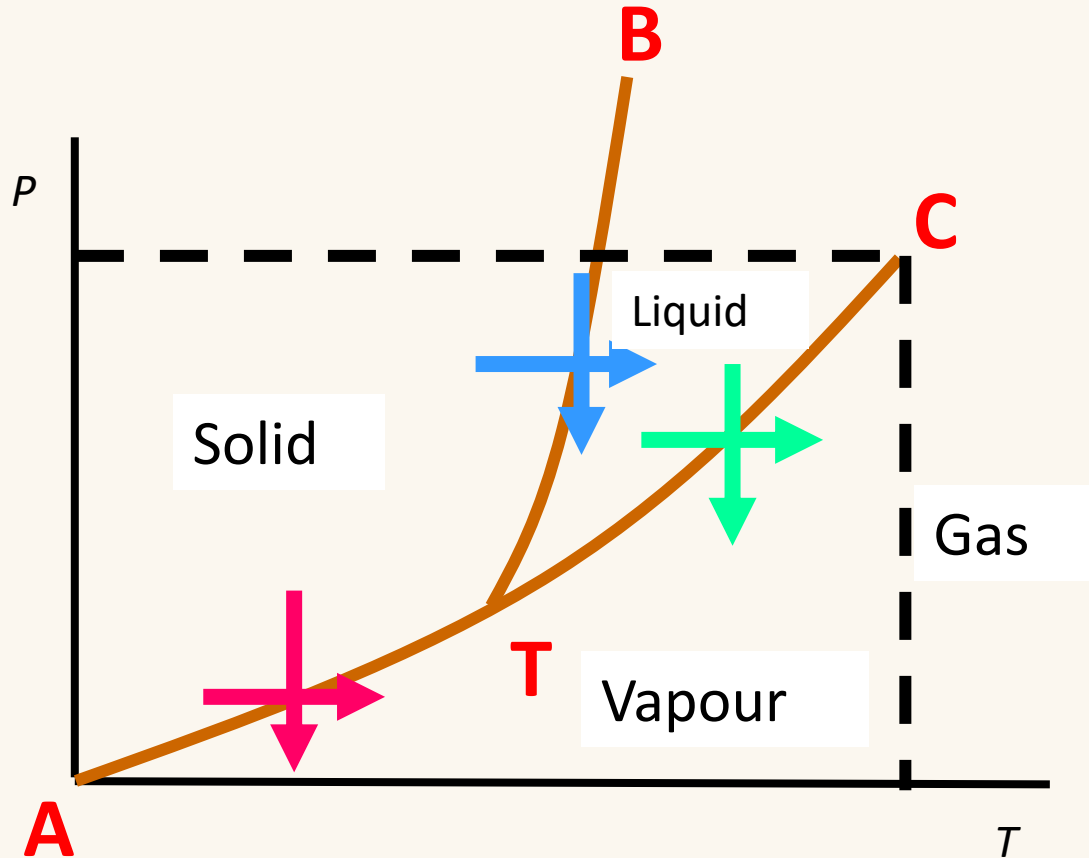(that expand on melting)

Triple Point T

Solid, liquid and vapour in equilibrium.

Critical Point C

Line TC shows saturated vapour pressure (SVP) with temperature.

At temperatures above T_C the vapour is called a gas, and cannot be liquefied by increasing pressure.

Phase Diagrams

Phase diagram for most substances
(that expand on melting)
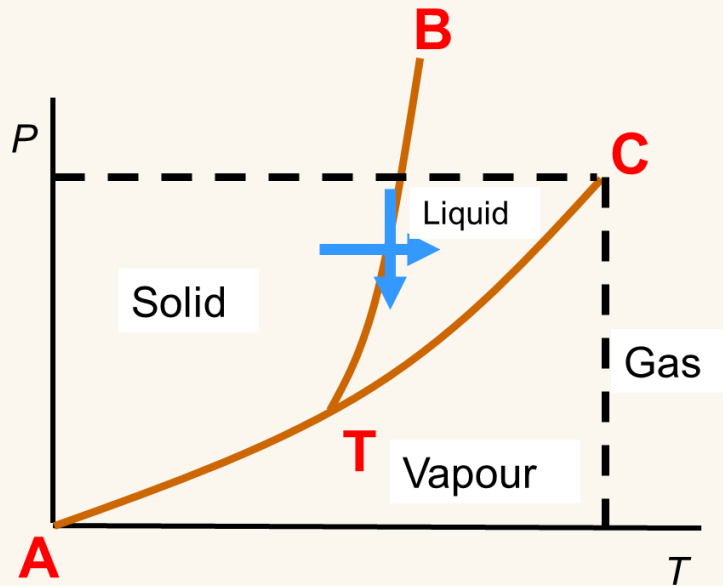
Phase transitions:

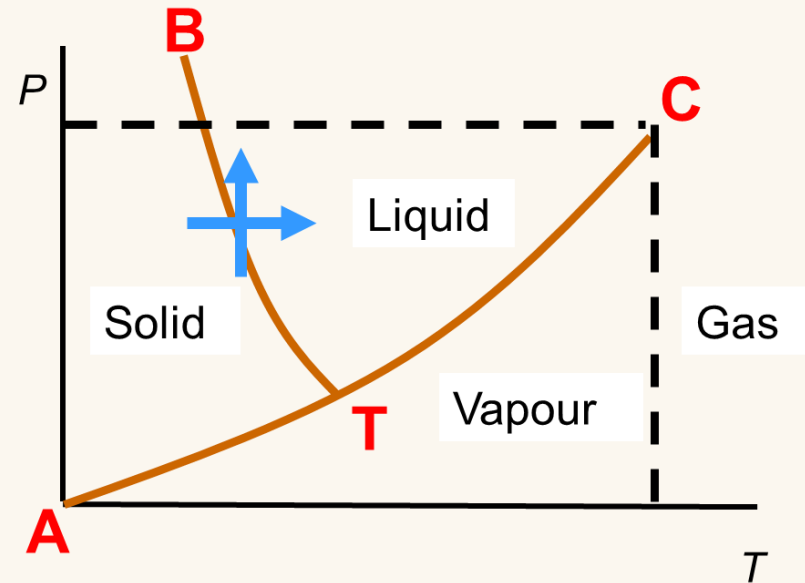MELTING (fusion)   Solid $\rightarrow$ liquid

BOILING (vaporisation)   liquid $\rightarrow$ vapour

SUBLIMATION   Solid $\rightarrow$ vapour

Phase diagram for water

Phase diagram for most substances (that expand on melting)

Phase diagram for water

Water is unusual in that TB has a negative slope. This means the melting temperature decreases with increasing pressure.
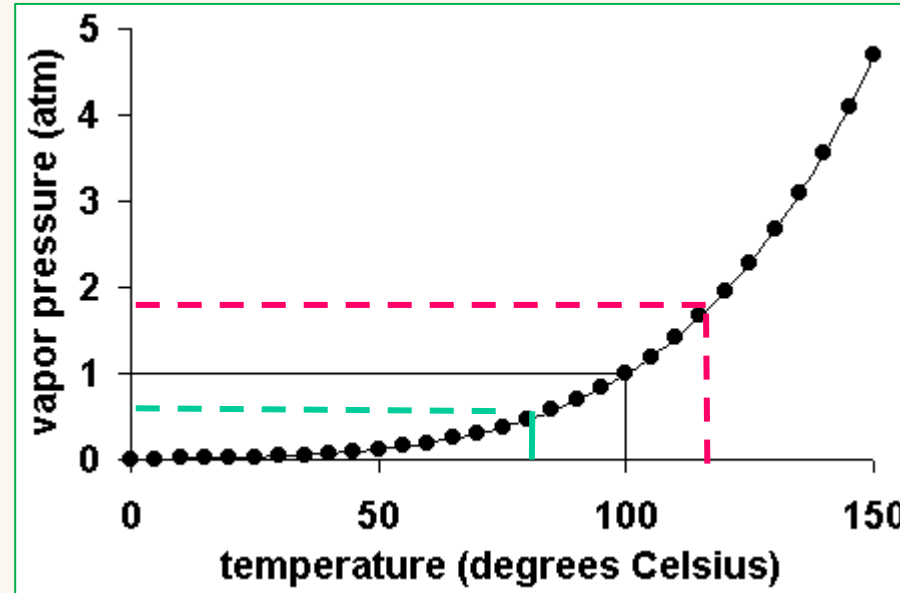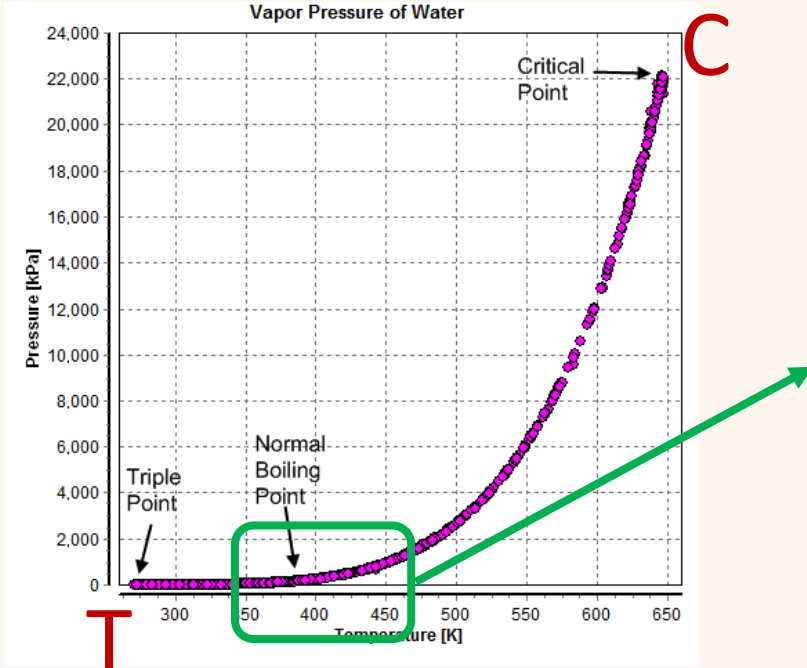
Boiling

Why is it not possible to make a good cup of tea at the top of Everest?

....because the water boils at less than 100°C

Boiling Point

Vapor Pressure of Water

At high altitude   P < 1 atm

water boils at T < 100°C

NORMAL BOILING POINT is the temperature at which the vapour pressure = 1 atm

In pressure cooker P > 1 atm

water boils at T > 100°C
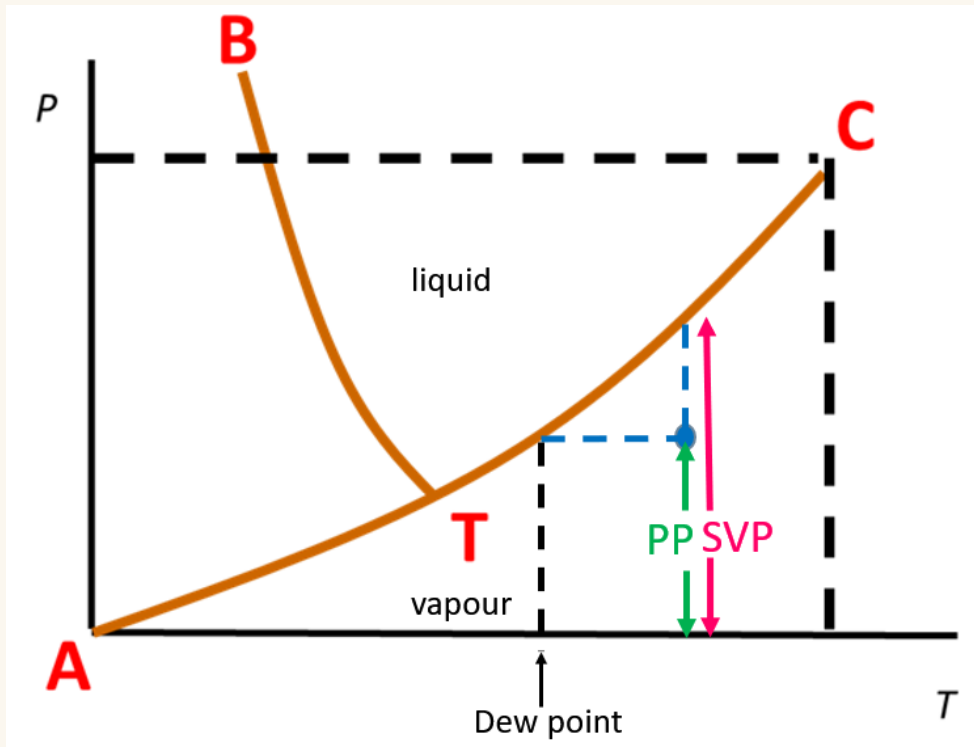
For water, vapour pressure = 1 atm at 373K (100°C)

Condensation
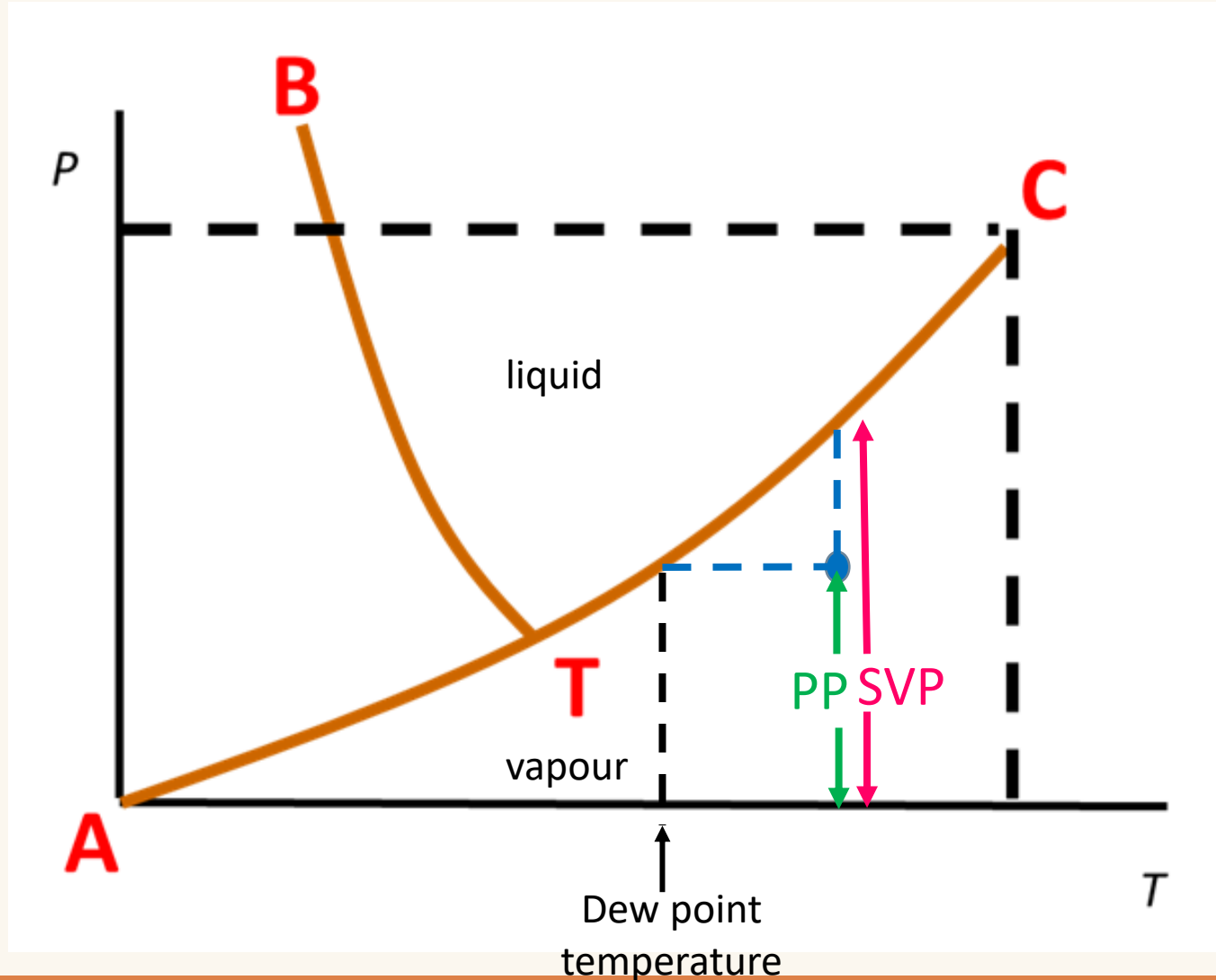
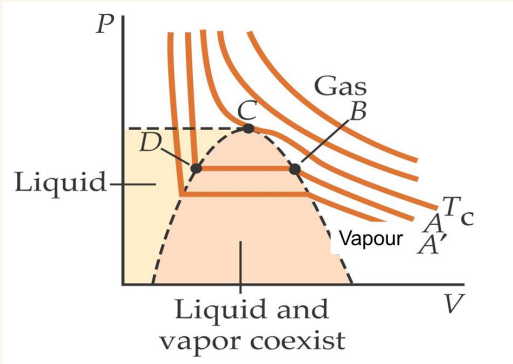Dew point is the temperature for which PP = SVP

Relative Humidity

$$Relative\ Humidity = \frac{Partial\ pressure\ H_2O}{saturation\ vapour\ pressure\ of\ H_2O} \times 100\%$$

$$RH = \left(\frac{PP}{SVP}\right)_{at\ temp}$$
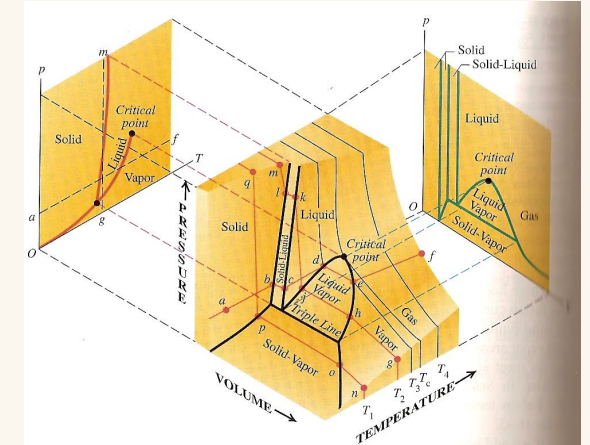
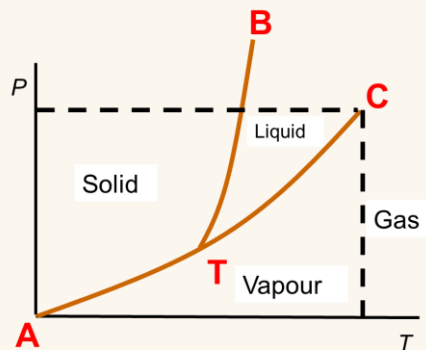Dew point is the temperature for which RH = 100%

Summary

$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT$$

Following assumptions of ideal gas break down:
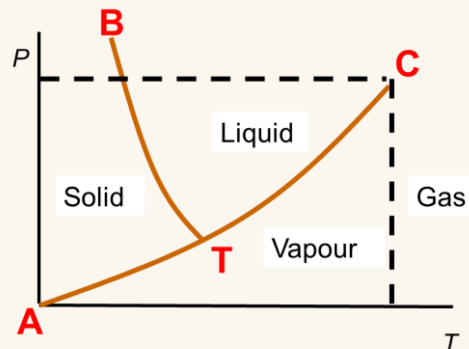- molecules well separated
- molecules exert no force on each other

For phase change: $Q = mL$

Substances that expand on melting

water

$$Relative\ Humidity = \frac{Partial\ pressure\ H_2O}{saturation\ vapour\ pressure\ of\ H_2O} \times 100\%$$

$$RH = \left(\frac{PP}{SVP}\right)_{at\ temp}$$

Critical temperature below which a vapour can be liquefied, above which a gas cannot be liquefied however high the pressure.

Normal boiling point is the temperature at which the vapour pressure = 1 atm

Dew point is the temperature for which RH = 100% (when PP = SVP)