

PROPERTIES OF PURE SUBSTANCE

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WHAT IS A PURE SUBSTANCE?

It is the substance that has a fixed and uniform chemical composition in all substance phases. An example of pure substance is pure water where it could be liquid, vapor or ice but in all it has the same chemical formula (H_2O).

Air may also be considered as a pure substance as long as it consists of 21% O_2 and 79% N_2 by volume. Sometimes CO_2 may be present in air in small traces.

PHASE EQUILIBRIUM in a PURE SUBSTANCE

There are three phases for each pure substance which are solid, liquid and gas phases. The pure substance may exist in one, two phases or three phases at the same time. Sometimes the phases may exist in equilibrium at the same time depending on the prevailing pressure and temperature. The pure substance changes from one phase to another at a certain pressure and a certain temperature and these conditions depend on the type of pure substance.

We will consider the phase change of pure water as an example since it can be noticed at normal pressure and temperature.

The change of phase of a pure substance is studied by following the changes in its thermodynamic properties. The most important thermodynamic properties are: pressure, temperature, volume, entropy, internal energy, enthalpy, density and specific volume.

Let us consider the phase change of 1 kg of pure water contained in a system that keeps the pressure constant during heating. Let this pure water be heated at constant pressure of 0.1 MPa from a temperature of 20 °C. We will notice that the temperature increases significantly as heating proceeds while the volume remains almost constant (insignificant increase) as long as the water is liquid. The water remains liquid until the temperature reaches 99.6 °C (the pressure and volume remain constant). At these conditions the pure water is known as saturated liquid. If the heating process continues the liquid water starts boiling and change of phase begins where the liquid changes gradually to vapor until all liquid is vaporized. At this point the vapor is known as saturated vapor. The change from saturated liquid to saturated vapor is known as change of phase process. During the change of phase the pressure and temperature remain constant while the volume increases significantly. When the heating continues the temperature rises again. Fig 2.1 shows this heating process.

The temperature and pressure at which the change of phase occurs are known as the saturation temperature and saturation pressure respectively. For example at a pressure of 0.1 MPa (1 bar) the saturation temperature is 99.6 °C and at a temperature of 99.6 °C the saturation pressure is 0.1 MPa. Fig 2.2 shows the relation between saturation pressure and saturation temperature.

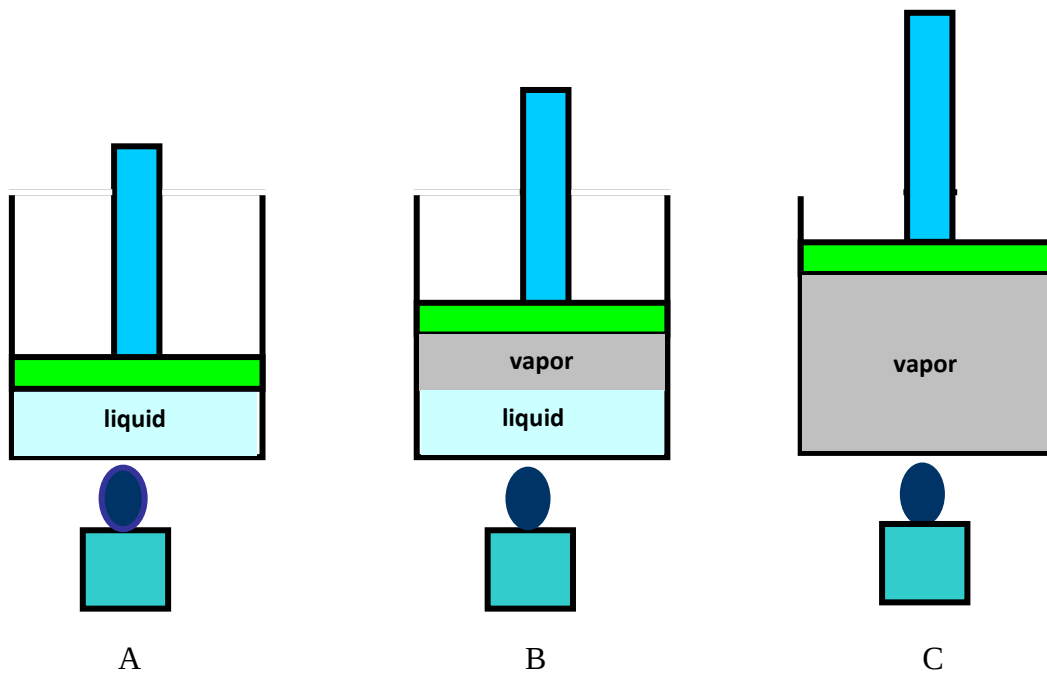


Fig 2.1

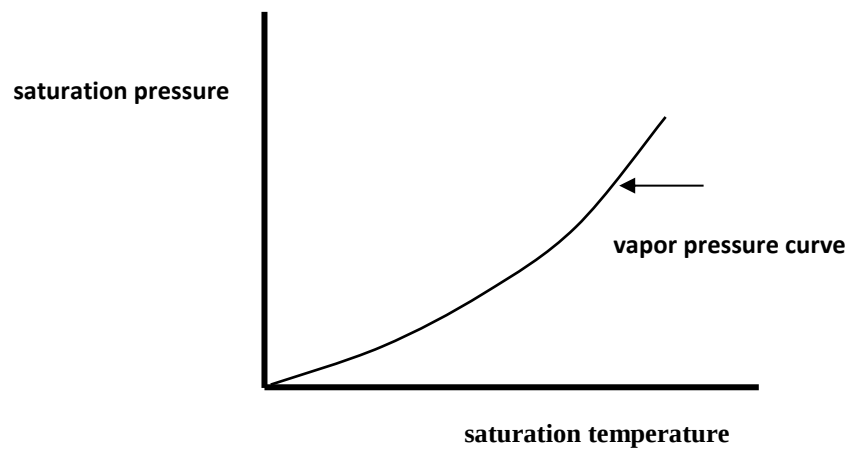


Fig 2.2

We can conclude from the previous experiment that the pure substance exists in two phase at the same time during the boiling (evaporation) process. The previous heating process can be represented by a line on the T-V diagram (line ABCD) and this line is known as the constant pressure line (isobaric line) as shown in fig 2.3.

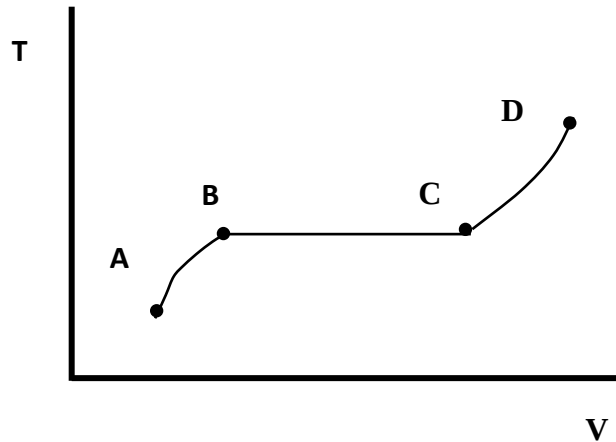


Fig 2.3

The segment AB represents the sensible heating process or heating of the liquid phase from initial temperature to the saturation temperature while the volume remains almost constant. The segment BC represents the evaporation process (change of phase process from saturated liquid to saturated vapor) where there is a significant increase in volume while the pressure and temperature remain constant. When the saturated vapor is further heated its volume and temperature rise and becomes superheated vapor. This process is represented by segment CD.

When the heating process is repeated but at different pressures similar paths to line ABCD are obtained as shown in fig 3.4.

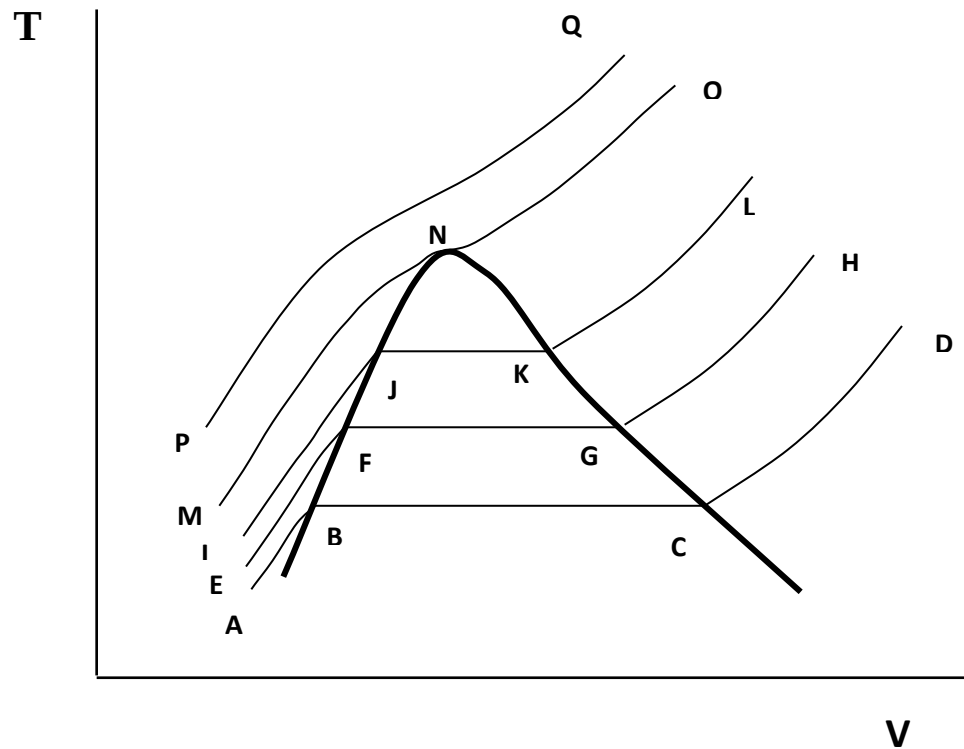


Fig 2.4

The line that joins the saturated liquid points at different pressures (line BFJN) is known as the saturated liquid line and the line that joins the saturated vapor points at different pressures (line CGKN) is known as the saturated vapor line. Both the saturated liquid line and the saturated vapor line meet at point N which is known as the CRITICAL POINT (there is a unique critical point for each pure substance). All thermodynamic properties of the pure substance at this point are known as the critical properties such as critical pressure, critical temperature, critical volume.....etc. Conditions at point vary from one pure substance to another.

At the critical point the thermodynamic properties of the saturated liquid state are the same as that of the saturated vapor state. This means that the saturated liquid changes to saturated vapor without heating.

When the pure substance is heated at a pressure higher than the critical pressure it changes from compressed liquid to superheated vapor directly without passing through the mixed phase state. This process is represented by line PQ on the T-V diagram shown in fig 2.4. Three distinct regions can be identified in fig 2.4. The first region to the left of the saturated liquid line which is the liquid phase region where the substance is liquid. The second region is between the saturated liquid line and the saturated vapor line which is the mixed phase region where the pure substance is a mixture of saturated liquid and saturated vapor. The third region is to the right of the saturated vapor line which is the vapor phase region and the vapor is superheated.

We can identify two types of liquid according to prevailing pressure and temperature.

1-The saturated liquid which is the liquid whose temperature equals the saturation temperature at applied pressure OR the liquid whose pressure equals the saturation pressure at liquid temperature.

2-The compressed liquid which is the liquid whose pressure is higher than the saturation pressure at liquid temperature. It is also known as the sub-cooled liquid since its temperature is lower than the saturation temperature at the applied pressure.

Table 2.1 shows three critical properties for some pure substances.

Table 2.1 Critical Point Conditions

Pure substance	Critical temperature °C	Critical pressure MPa	Critical specific volume m ³ /kg
water	374.14	22.09	0.003155
carbon dioxide	31.05	7.39	0.002143
oxygen	-118.35	5.08	0.002438
hydrogen	-239.85	1.3	0.032192
ammonia	132.5	11.2626	0.004252
nitrogen	-146.8	3.3899	0.0032087
helium	-267.7	0.22869	0.014441
argon	-122	4.85717	0.0018755

Let the heating process be performed for 1 kg of ice (solid phase of pure water) at constant pressure of 0.1 MPa (1 bar) starting from -10 °C. As the heating process proceeds there is a significant rise in temperature but little change in volume until the temperature reaches 0 °C. At this temperature the ice starts melting and it is known as saturated solid. The temperature remains constant until all the ice is melt completely and becomes liquid. It must be mentioned that for water (an exception of all other pure substances) the volume of the melted liquid is less than the volume of the saturated solid which means that that density of ice is less than the density of liquid. As heating continues the phase changes occur as mentioned earlier.

Let the heating process of 1 kg of ice be performed at a constant pressure of 0.26 kPa starting from -20 °C. As the heating continues very little change in volume is noticed but significant rise in temperature occurs until -10 °C. At this temperature the ice converts directly to saturated vapor without passing through the liquid phase. This process is known as the sublimation process. Any further heating converts the vapor to superheated vapor.

Let the heating process of 1 kg of ice be performed at a constant pressure of 0.6113 kPa starting from -10 °C. As the heating process proceeds little change in volume is noticed and significant rise in temperature occurs until 0.01 °C. If the heating process continues some of the ice becomes liquid and some becomes vapor and some remains ice. At these conditions the three phases exist at the same time in equilibrium and this state is known as the triple point state or simply TRIPLE POINT. So for pure water the triple point conditions are 0.6113 kPa and 0.01 °C. For each pure substance there is a unique triple point. All other pure substances in nature follow the same behavior as pure water during heating process but at different conditions of pressure and temperature. Table 2.2 shows the triple point conditions for some pure substances and fig 2.5 shows the P-T diagram for a pure substance.

Table 2.2 Triple Point Conditions

Type of pure substance	Triple point temperature °C	Triple point pressure kPa
hydrogen	-259	7.194
oxygen	-219	0.15
nitrogen	-210	12.53
mercury	-39	0.00000013
water	0.01	0.6113
zinc	419	5.066
silver	961	0.01
copper	1038	0.000079

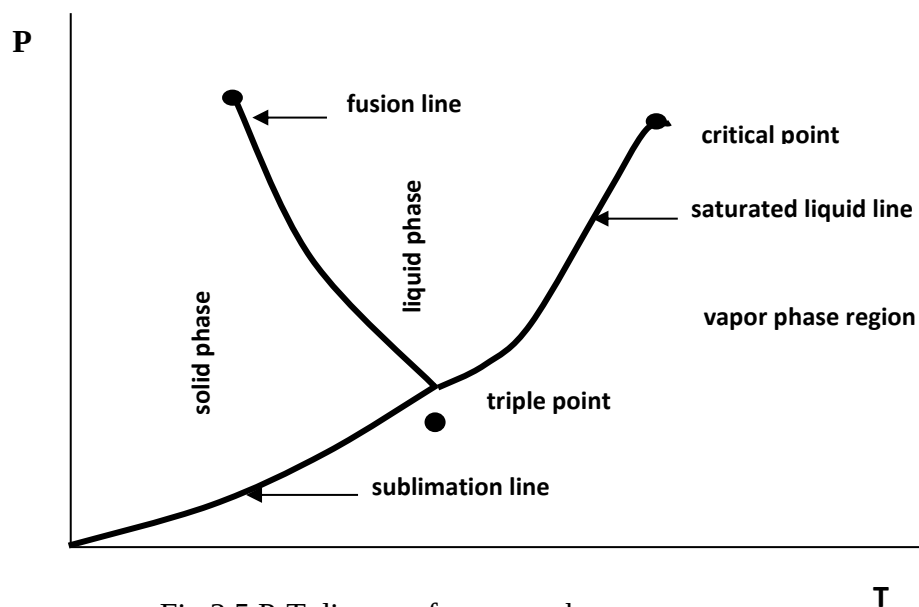


Fig 2.5 P-T diagram for pure substance

When the superheated vapor is heated to very high temperature it becomes gas. So the gas is defined as “highly superheated vapor”.

The highly superheated vapor becomes gas when the relation between its pressure, volume and temperature follows the following equation.

$$PV = mRT \quad (2.1)$$

OR per unit mass

$$Pv = RT \quad (2.2)$$

where,

P=pressure (Pa)

V=total volume (m³)

v=specific volume (m³/kg)

m=mass (kg)

T=absolute temperature (K)

R=specific gas constant (J/kg/K)

This equation is the equation of state for the perfect gas and cannot be used for any vapor.

The equation of state is written in another form which is,

$$PV = nR_oT \quad (2.3)$$

OR per unit mole

$$Pv = R_oT \quad (2.4)$$

Where,

n=number of moles

R_o=universal gas constant= 8314.5 J/kmole K

$$n = \frac{m}{MW} \quad (2.5)$$

Where,

MW=molecular weight

$$PV = \frac{m}{MW} R_oT = PV = m \frac{R_o}{MW} T$$

$$\therefore R = \frac{R_o}{MW} \quad (2.6)$$

Equation (2.4) can be written as,

$$\frac{Pv}{T} = R_o = \textit{Constant (C)}$$

We can write,

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \tag{2.7}$$