5.0 WORKING SUBSTANCE QUALITY

Working fluid: This can be defined as the matter contained within the boundaries of a thermodynamic system. The working fluid in a thermodynamic system could be in solid, liquid or gaseous phase or a combination of the phases.

5.1 Phase and Pure Substance

Phase: refers to a quantity of matter that is homogeneous throughout in both chemical composition and physical structure.

> Three common phases: solids, liquids and gases

Solids: molecules closely packed, high molecular forces, definite shape and volume **Liquids**: molecules less closely packed, weaker molecular forces, fluid shape and definite volume

Gases: molecules move around, weakest molecular forces, no shape and containerdefined volume

Phase change types:

- > Condensation: this is a process whereby gas changes into a liquid.
- > **Vaporization**: this is a process whereby liquid changes to gas.
- **Freezing**: this is a process where liquid changes to solid.
- > Melting (fusion): this is a process where a solid changes into liquid.
- > Sublimation: this is a process where a solid changes to gas without becoming liquid.
- > **Deposition**: this is a process where a gas changes to solid without becoming liquid.

Homogeneity in Physical Structure means that the matter is all solid, or all liquid, or all vapour. A system can contain one or more phases.

A **Pure Substance:** is one that is uniform and invariable in chemical composition. A pure substance can exist in more than one phase which is called **mixed phase**, but its chemical composition must be the same in each phase.



Figure 1: P-V-T Surface for a Pure Substance

From the diagram in figure 1, we can see that water can exist as a solid, liquid or in gaseous (vapour) form. It can also be seen that a pure substance can exist in solid-vapour, solid-liquid, liquid vapour and solid-liquid-vapour (Triple line).

Consider the processes involved in heat water at a constant pressure of 1 atm from an initial temperature of 20 °C. As shown in figure 2, the heating takes place in a piston-cylinder device where a fixed weight is placed to keep the pressure of the water constant. PROCESS 1-2:

As the liquid is heated at constant pressure, the temperature and specific volume will increase from the subcooled liquid state or compressed liquid state to the saturated liquid state.

Note: The properties of the liquid at the compressed liquid region are approximately equal to the properties at the saturated region/state.



Figure 2: a piston-cylinder device at the initial state

PROCESS 2-3

The liquid attains a set temperature and begins to boil. This is called the SATURATION TEMPERATURE and the liquid is said to exist as SATURATED LIQUID. The properties of the liquid are denoted with the subscript f e.g. $V_2 = V_f$. While temperature and pressure remains constant, phase change takes place (water boils at 100 °C and 1 atm). At state 3, the liquid and vapour phase are in equilibrium.



Figure 3: a piston-cylinder device at saturated temperature

STATE 3
P = 1 atm $T = 100^{\circ}$ C
Heat

Figure 4: a piston-cylinder device with liquid and vapour phase at equilibrium PROCESS 3-4

At state 4, vaporization is complete and only saturated vapour exists. The subscript g e.g. $V_4 = V_g$ is used to denote the properties at this region.



Figure 5: a piston-cylinder device with saturated vapour

Note: In the saturation region the temperature and pressure are dependent properties; if one is known, then the other is automatically known.

PROCESS 4-5:

If the heating is sustained, the temperature rises above the saturation temperature (100 °C), the volume also increases. Another state is reached (state 5), known as the superheated state. The properties at this region are found in the superheated section of the steam table.



Figure 6: a piston-cylinder device with superheated vapour

The processes illustrated above can be represented with figure 7 below.



Figure 7: process constant pressure lines





A saturated liquid and vapour lines are established when all the saturated liquid and vapour states are connected respectively. The saturated liquid and vapour lines intersect at the critical point and form what is known as the "Steam Dome". The region between the saturated liquid and vapour lines is known as the "SATURATED LIQUID-VAPOUR MIXTURE REGION" (WET REGION (i.e. a mixture of saturated liquid and vapour mixture) as shown in figure 9.



Figure 9: T-V Diagram of the saturated liquid and vapour lines (Steam Dome)



Figure 10: P-v Diagram of the saturated liquid and vapour lines (Steam Dome)

5.2 THIRD LAW OF THERMODYNAMIC

Third Law of Thermodynamic

The third law states that the entropy of a pure crystalline substance is zero at the absolute zero of temperature, 0 K or 0°R. Substances not having a pure crystalline structure have a nonzero value of entropy at absolute zero.