LECTURE 4

The State Postulate

The state of the system is described by its properties.

Once a sufficient number of properties are specified, the rest of the properties assume some values automatically.

The number of properties required to fix a state of a system is given by the **state postulate**:

The state of a simple compressible system is completely specified by two independent, intensive properties.

The system is called a **simple compressible system** in the absence of electrical, magnetic, gravitational, motion, and surface tension effects.

The state postulate requires that the two properties specified be independent to fix the state.

Two properties are independent if one property can be varied while the other one is held constant.

Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system.

Thus, temperature and pressure are not sufficient to fix the state of a two-phase system.

Otherwise an additional property needs to be specified for each effect that is significant.

An additional property needs to be specified for each other effect that is significant.

Zeroth Law of Thermodynamics

We cannot assign numerical values to temperatures based on our sensations alone. Furthermore, our senses may be misleading.

Several properties of material changes with temperature in a repeatable and predictable way, and this forms the basis of accurate temperature measurement.

The commonly used mercury-in-glass thermometer for example, is based on the expansion of mercury with temperature.

Temperature is also measured by using several other temperature dependant properties.

Two bodies (eg. Two copper blocks) in contact attain thermal equilibrium when the heat transfer between them stops.

The equality of temperature is the only requirement for thermal equilibrium.

The **Zeroth Law of Thermodynamics**

If two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.

This obvious fact cannot be concluded from the other laws of thermodynamics, and it serves as a basis of temperature measurement.

By replacing the third body with a thermometer, the zeroth law can be restated *two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact*

The zeroth law was first formulated and labeled by R.H. Fowler in 1931.

Temperature Scales

All temperature scales are based on some easily reproducible states such as the freezing and boiling point of water, which are also called the **ice-point** and the **steam-point** respectively.

A mixture of ice and water that is in equilibrium with air saturated with water vapour at 1atm pressure, is said to be at the ice-point, and a mixture of liquid water and water vapour (with no air) in equilibrium at 1atm is said to be at the steam-point.

Celsius and Fahrenheit scales are based on these two points (although the value assigned to these two values are different) and are referred as two-point scales.

In thermodynamics, it is very desirable to have a temperature scale that is independent of the properties of the substance or substances.

Such a temperature scale is called a **thermodynamic temperature scale**.(Kelvin in SI)

Ideal gas temperature scale

The temperatures on this scale are measured using a constant volume thermometer.

Based on the principle that at low pressure, the temperature of the gas is proportional to its pressure at constant volume.

The relationship between the temperature and pressure of the gas in the vessel can be expressed as

$$T = a + b.P$$

Where the values of the constants *a* and *b* for a gas thermometer are determined experimentally.

Once *a* and *b* are known, the temperature of a medium can be calculated from the relation above by immersing the rigid vessel of the gas thermometer into the medium and measuring the gas pressure.

Ideal gas temperature scale can be developed by measuring the pressures of the gas in the vessel at two reproducible points (such as the ice and steam points) and assigning suitable values to temperatures those two points.

Considering that only one straight line passes through two fixed points on a plane, these two measurements are sufficient to determine the constants *a* and *b* in the above equation.

If the ice and the steam points are assigned the values 0 and 100 respectively, then the gas temperature scale will be identical to the Celsius scale.

In this case, the value of the constant *a* (that corresponds to an absolute pressure of zero) is determined to be $–273.15^0$C when extrapolated.

The equation reduces to T = bP, and thus we need to specify the temperature at only one point to define an absolute gas temperature scale.

Absolute gas temperature is identical to thermodynamic temperature in the temperature range in which the gas thermometer can be used.

We can view that thermodynamic temperature scale at this point as an absolute gas temperature scale that utilizes an ideal gas that always acts as a low-pressure gas regardless of the temperature.

At the Tenth international conference on weights and measures in 1954, the Celsius scale has been redefined in terms of a single fixed point and the absolute temperature scale.

The triple point occurs at a fixed temperature and pressure for a specified substance.

The selected single point is the **triple point** of water (the state in which all three phases of water coexist in equilibrium), which is assigned the value 0.01 C. As before the boiling point of water at 1 atm. Pressure is 100.0 C. Thus the new Celsius scale is essentially the same as the old one.

On the Kelvin scale, the size of Kelvin unit is defined as “ the fraction of 1/273.16 of the thermodynamic temperature of the triple point of water, which is assigned a value of 273.16K”. The ice point on Celsius and Kelvin are respectively 0 and 273.15 K.