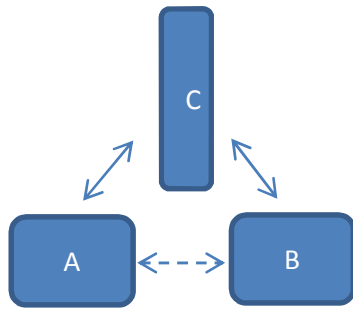


## Lecture 2

### Thermal equilibrium

When a hot body A and a cold body B are brought together then heat flows from the body A to body B until both attain the same temperature. Now the body A and body B are said to be in **thermal equilibrium**. The requirement for thermal equilibrium is the **equality of temperature**.

### Zeroth law of thermodynamics



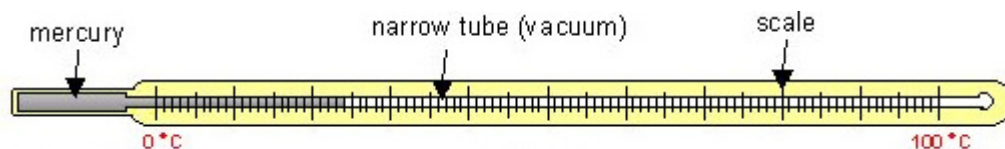
It states that if two bodies (A and B) are in thermal equilibrium with a third body (C), then they are also in thermal equilibrium with each other.

Zeroth law serves as the basis for temperature measurement. If the third body C is replaced with a thermometer then both with A and B it shows the same temperature reading.

For making a **thermometer**, we should have

- a substance with a measurable property (called **thermometric property**) that changes with temperature. The substance that exhibits thermometric property is called a **thermometric substance**
- a **temperature scale** to read the value of temperature

For eg. in a liquid in glass thermometer the thermometric property is length (length of mercury column changes with temperature)



### Temperature scales

For a temperature scale we should have

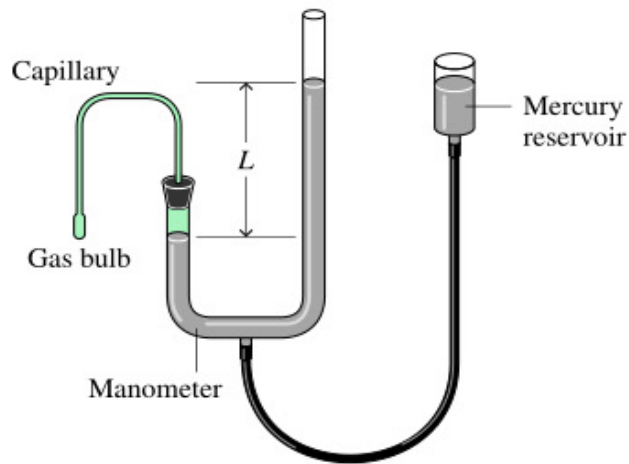
- Reference points (or fixed points) (freezing of water assigned as 0°C and boiling of water assigned as 100°C are the reference points in the thermometer shown above)
- Interpolation scheme (how to divide the length between 0°C and 100°C so that we get the intermediate temperatures. Here a linear interpolation is used).

The temperature scales used in the SI and in the English system today are the **Celsius** scale and the **Fahrenheit** scale, respectively. On the Celsius scale, the ice and steam points were originally assigned the values of 0 and 100°C, respectively. The corresponding values on the Fahrenheit scale are 32 and 212°F. These are often referred to as **two-point scales** since temperature values are assigned at two different points.

It is very desirable to have a temperature scale that is *independent of the properties of any substances*. Such a temperature scale is called a **thermodynamic temperature scale**. The thermodynamic temperature scale in the SI is the **Kelvin scale**.

## Constant volume gas thermometer and the Ideal gas temperature scale

A temperature scale that is nearly identical to the Kelvin scale is the **ideal-gas temperature scale**. The temperatures on this scale are measured using a **constant-volume gas thermometer**



**Thermometric substance:** Gas in the bulb

**Thermometric property:** **Pressure** exerted by the gas

The pressure exerted by the gas, at a particular temperature, is measured by an open-tube mercury manometer. As temperature increases, the gas expands, forcing mercury up in the open tube. The gas is kept at constant volume by raising or lowering the reservoir.

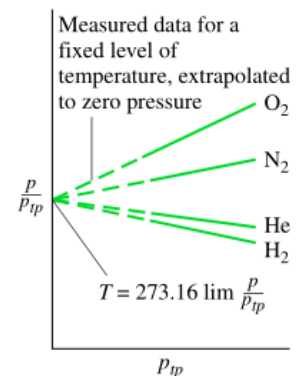
Let  $p$  stand for the pressure in a constant-volume gas thermometer when the gas is maintained at temperature  $T$ . Temperature value can be specified very simply by a linear relation

$$T = \alpha p$$

The value of  $\alpha$  may be determined by inserting the thermometer into a bath maintained at a standard fixed point, the triple point of water. Measure the pressure; call it  $p_{tp}$ , of the gas at the triple point temperature, 273.16 K

$$\text{Therefore, } \alpha = \frac{273.16}{p_{tp}}$$

$$\text{Temperature, } T = 273.16 \frac{p}{p_{tp}}$$



But both  $p$  and  $p_{tp}$  depends on the **amount of gas** and the **type of gas** used. So we get different values of temperature when either the amount of gas or the type of gas is changed. To overcome this difficulty measurements (with original temperature and the reference temperature) are made successively by reducing the amount of gas in the bulb. When the values of  $p_{tp}$  and  $\frac{p}{p_{tp}}$  from these measurements are plotted and the curves extrapolated to where  $p_{tp} \rightarrow 0$ , the  $\frac{p}{p_{tp}}$  values from thermometers with different gases approach one another, and in the **limit** as pressure tends to zero, the same value for  $\frac{p}{p_{tp}}$  is obtained for each gas.

Now **the gas temperature scale** may be defined as

$$T = 273.16 \lim_{p_{tp} \rightarrow 0} \frac{p}{p_{tp}}$$

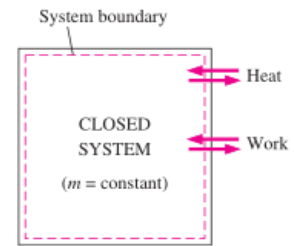
where “lim” means that both  $p$  and  $p_{tp}$  tend to zero

This gas temperature scale can be called as an **ideal gas temperature scale** since, as pressure tends to zero the gas behaves as an ideal gas.

## Heat and Work

Energy can cross the boundary of a closed system in two forms: **heat** and **work**

**Heat** is defined as the form of energy that is transferred between two systems (or a system and its surroundings) by virtue of a temperature difference



Thermodynamic definition of work:

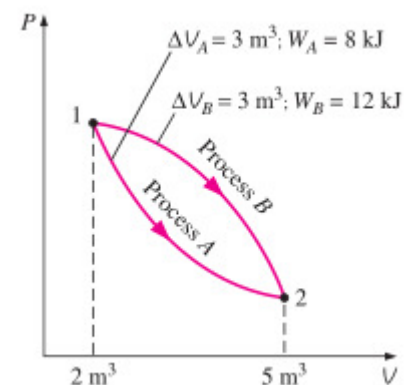
**Work** is done by a system on its surroundings if the sole effect on everything external to the system could have been the raising of a weight.

**Sign convention** for heat and work interactions: heat transfer to a system and work done by a system are positive; heat transfer from a system and work done on a system are negative.

### Point functions (State functions)

They depend on the **state** only, and not on how a system reaches that state. Thermodynamic properties are point functions. Point functions are **exact differentials**, i.e. change in a property during a process only depends on the end states (not the path). For eg. Change in volume during a process can be evaluated as

$\int_1^2 dV = V_2 - V_1$ , where  $V_2$  and  $V_1$  are the volume at the end states of a process



Also  $\oint dV = 0$ , i.e. the change in volume for the whole cycle is zero, since initial state and final state are the same. This is true for any property. **Cyclic integral of any property is zero.**

### Path functions

Path functions have **inexact differentials**. Eg. Heat and work. A differential amount of heat or work is said to be **inexact** because, to evaluate the integral the **path** of the process has to be specified. So heat and work are **not properties** (point functions) of a system. They are path functions. Inexact differentials are denoted by a symbol  $\delta$ .

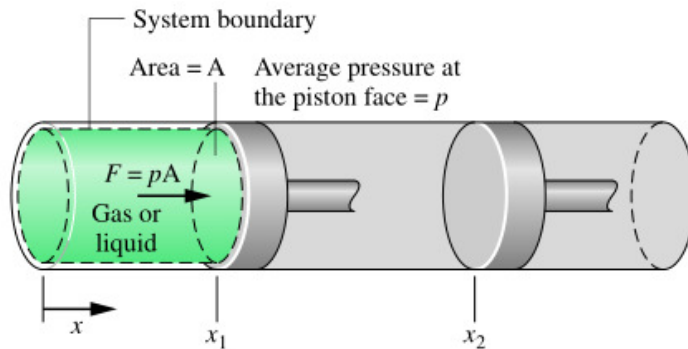
$$\int_1^2 \delta W \neq W_2 - W_1$$

### Heat and work: Similarities

- Both are recognized at the boundaries of a system as they cross the boundaries. That is, both heat and work are boundary phenomena.
- Systems possess energy, but not heat or work.
- Both are associated with a process, not a state. Unlike properties, heat or work has no meaning at a state.
- Both are path functions (i.e., their magnitudes depend on the path followed during a process as well as the end states).

## Expansion Work (displacement work)

Expansion work is the work done by a closed system as the boundary moves (expands). For eg. The work done by the gas contained in a piston–cylinder assembly as the gas expands is expansion work.



$$W = \int_1^2 dW = \int_1^2 F dx = \int_1^2 p A dx$$

$$A dx = dV$$

$$W = \int_1^2 p dV$$

The integral can be evaluated when the relationship between  $p$  and  $V$  are specified. When the relationship is specified as  $pV^n = \text{constant}$ , the process is termed as a **polytropic process**.

**Note:** Work done,  $W = \int p_{\text{external}} dv$ , but for a quasi-static process  $p_{\text{external}} = p_{\text{system}}$

Therefore for a quasi-static process  $W = \int_1^2 p dV$ , where  $p$  = pressure of the system

Isobaric process ( $p = \text{constant}$ )

$$W = \int_1^2 p dV = p(V_2 - V_1)$$

Isothermal process ( $pV = \text{constant}$ )

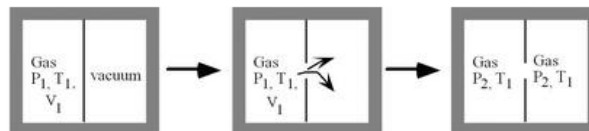
Assuming the gas as ideal gas. ( $pV = mRT$ )

$$pV = p_1 V_1 = p_2 V_2 = \text{constant}, c \implies p = \frac{c}{V} \implies W = \int_1^2 p dV = \int_1^2 c \frac{dV}{V} = p_1 V_1 \ln \frac{V_2}{V_1}$$

Polytropic process

$$pV^n = p_1 V_1^n = p_2 V_2^n = \text{constant}, c \implies p = \frac{c}{V^n} \implies W = \int_1^2 p dV = \int_1^2 c \frac{dV}{V^n} = \frac{p_2 V_2 - p_1 V_1}{1-n}$$

Free expansion (Unrestrained expansion, expansion against vacuum) Work done = 0



Here unrestrained expansion is not a quasi-static process, it is an irreversible process.

Work done,  $W = \int p_{\text{external}} dv$ , and  $p_{\text{external}} = 0$  (For vacuum, pressure = 0)

Therefore  $W = 0$ .