

ZEROth LAW OF THERMODYNAMICS AND TEMPERATURE

The concept of temperature originated in man's primitive perception of hot and cold. These perceptions are not of course analytical. The definition of temperature is a consequence of the zeroth law of thermodynamics.

Concept of thermal equilibrium: let a simple homogeneous system of constant mass be considered, for example some amount of gas confined in a chamber of fixed volume. For a given composition of gas, its pressure (P) and volume (V) is sufficient to specify its thermodynamic state in equilibrium. The P and V are independent variables, i.e. if volume is kept constant, the pressure can vary widely over a range of values and vice versa. Let two such systems 'A' and 'B' be considered, each being enclosed walls (Fig. 2.1a). Being isolated systems, 'A' and 'B' do not interact with each and the surroundings. Each will be individually in a state of thermodynamic equilibrium. 'A' is characterized by pressure ' P_{Ai} ' and volume ' V_{Ai} ' and the corresponding quantities for 'B' are ' P_{Bi} ' and ' V_{Bi} '

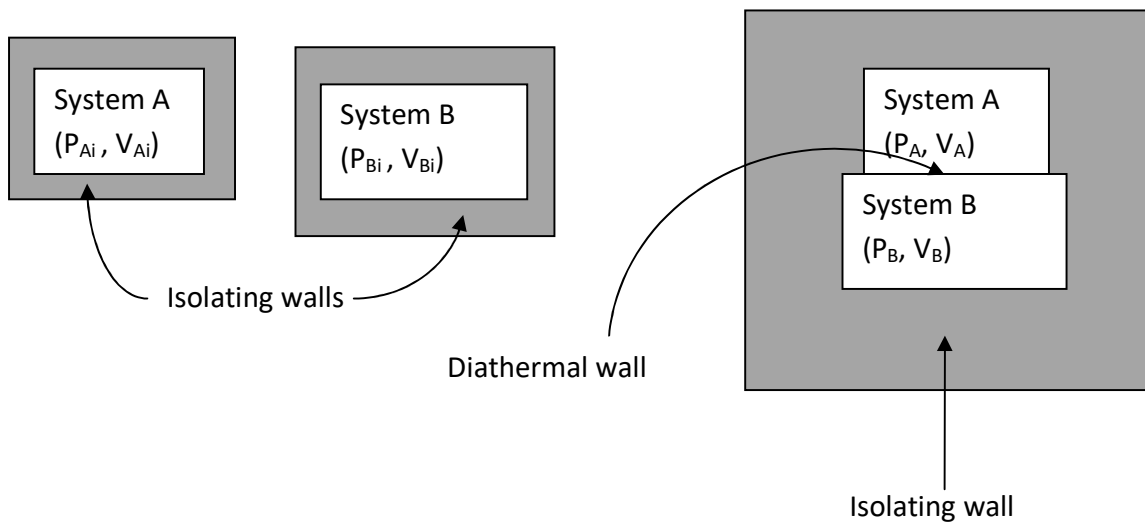


Fig. 2.1 (a) A and B isolated from each other.

Fig. 2.1 (b) A and B in thermal contact

Next 'A' and 'B' are brought in thermal contact by means of a diathermal (allows only heat transfer through it) wall as in Fig.(2.1b) maintaining their isolation from the surroundings. Both systems will, in general undergo spontaneous changes in their physical properties, until the combined system 'A+B' attains a new state of equilibrium, when no further changes occur. Under such conditions there will no further net heat transfer between them and they are said to be in thermodynamic equilibrium.

Before they were thermally connected, 'A' and 'B' were isolated systems and two pairs of variables (P_{Ai}, V_{Ai}) and (P_{Bi}, V_{Bi}) respectively were required to describe the two systems

completely. When in thermal equilibrium, the corresponding values are (P_A, V_A) and (P_B, V_B) . So four coordinates are associated with the system 'A+B'. But 'a' and 'B' are no longer isolated. They form a single composite system 'A+B' with thermodynamic coordinates (P_A, V_A, P_B, V_B) . Out of this four coordinates if the values of three coordinates are maintained constant the fourth one will automatically be maintained constant. So there should be a single mathematical equation of state connecting the four variables denoted by:

$$\phi(P_A, V_A, P_B, V_B) = 0 \quad \dots\dots\dots(2.1)$$

Where ϕ is a functional form, which depends on the nature of 'A' and 'B'. This shows that out of the four variables any three can be independent, while the fourth one should on other three. So for two systems in thermal equilibrium and isolated from the surroundings, three thermodynamic coordinates are sufficient to describe it completely.

Zeroth law of thermodynamics

The Zeroth law states that if two systems 'A' and 'B' are separately in thermal equilibrium with a third system 'C', then they are also in thermal equilibrium with each other.

Let

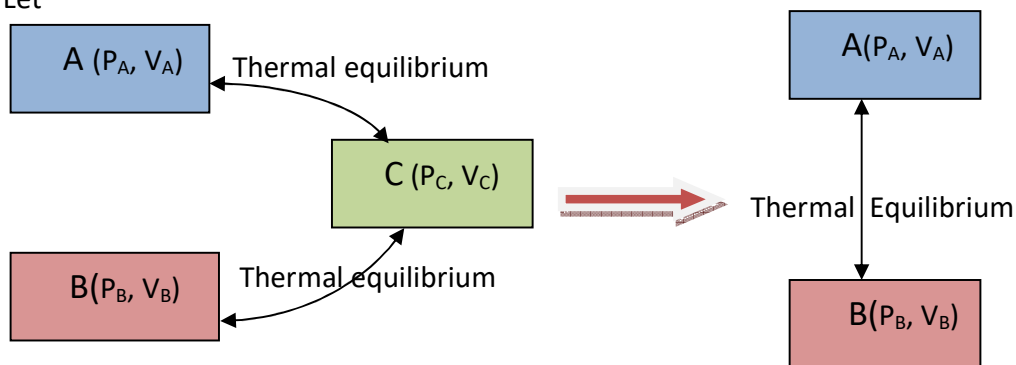


Fig. 2.2: Demonstration of Zeroth law of Thermodynamics.

Empirical temperature:

From the statement of Zeroth law it is clear that all three systems 'A' 'B' and 'C' being in thermal equilibrium with each other must have some property in common. This common property is identified as **temperature**. From equation (2.1), the condition under which the systems 'A' and 'C' are in thermal equilibrium is expressed by the equation:

$$\phi_1(P_A, V_A, P_C, V_C) = 0 \quad \dots\dots\dots(2.2)$$

So any one of these four coordinates can be expressed as a function of the other three.

Let $P_C = F_1(P_A, V_A, V_C)$ (2.3)

Where F_1 is another functional form.

Similarly for the system 'B' to be in thermal equilibrium with 'C' the condition is

$$P_C = F_2(P_B, V_B, V_C) \dots\dots\dots(2.4)$$

From equations (2.3) and (2.4)

$$F_1(P_A, V_A, V_C) = F_2(P_B, V_B, V_C) \dots\dots\dots(2.4)$$

So equation (2.4) denotes the thermal equilibrium of 'A' and 'B' with 'C'

If this is so, then the Zeroth Law demands that 'A' and 'B' must also be in thermal equilibrium with each other. Giving the corresponding equation as

$$\phi_3(P_A, V_A, P_B, V_B) = 0 \dots\dots\dots(2.5)$$

Equation (2.4) implies equation (2.5). Both are equivalent. But while equation (2.4) contains ' V_C ' equation (2.5) does not. It follows that ' F_1 ' and ' F_2 ' must contain ' V_C ' in such a form that it cancels out in equation (2.4), thus reducing the equation to:

$$f_1(P_A, V_A) = f_2(P_B, V_B) \dots\dots\dots(2.6)$$

{Of course with V_C cancelled, the functional form changes}

Applying the same argument, considering 'A' and 'C' separately in thermal equilibrium with 'B'

$$f_1(P_A, V_A) = f_3(P_C, V_C) \dots\dots\dots(2.6)$$

Hence $f_1(P_A, V_A) = f_2(P_B, V_B) = f_3(P_C, V_C) = \theta$(2.7)

This equation can also be extended to a large number of systems in thermal equilibrium with each other giving :

$$f_1(P_A, V_A) = f_2(P_B, V_B) = f_3(P_C, V_C) = f_4(P_D, V_D) = f_5(P_E, V_E) = \dots\dots\dots = \theta \dots\dots\dots(2.8)$$

Thus for every system, there exists a function of its state variable such that the numerical value of the function is same for all systems in thermal equilibrium with each other. The common value ' θ ' of these functions is called the **empirical temperature**. So, **temperature may be defined as function of state of a system, such that it takes the same value for all systems in thermal equilibrium with one another**. For a simple system $f(P,V) = \theta$ is called the equation of state.

Principle of Thermometry

The Zeroth law concludes that if two or more systems are in thermal equilibrium with each other they all have the same temperature. Out of the three systems 'A', 'B' and 'C' stated in the previous section, any one system suppose 'A' can be used to measure the temperature of others, provided 'A' has associated with it a temperature dependent parameter called **thermometric property**. To construct a temperature scale it is necessary :

- i. To express the temperature as an explicit function of the thermometric property.
- ii. to assign a numerical value to the temperature of some standard state of the chosen system. That standard state is called **fixed point**. **A fixed point is defined as an easily reproducible standard state of the thermometric substance.**

Step i) To express the temperature as an explicit function of the thermometric property.

Let 'A' be a fixed mass of gas of constant composition. The equation of state of such a system can be written as $f(P,V) = 0$. The parameters 'P' and 'V' are independent in absence of any constraints, but once the condition is imposed that 'A' has same temperature as 'C' the number of independent variables reduces to one. For a given pressure 'p' the volume 'V' is uniquely determined.

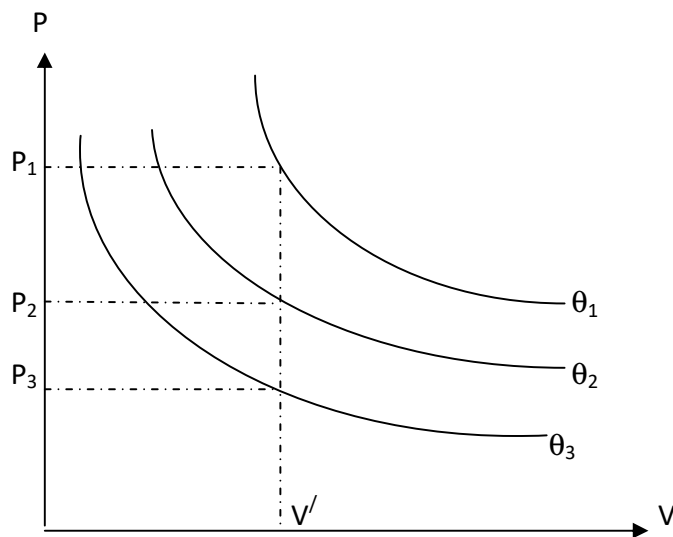


Fig.2.3: Isotherms of a gas at empirical temperatures θ_1 , θ_2 and θ_3 on a scale to be defined.

Fig. 2.3 shows the different (P,V) states of the system 'A' plotted on an indicator diagram at the same empirical temperature θ of 'C'. This plot is called an isotherm. The figure shows three isotherms for different temperatures of 'C'. The volume and pressure of a gas are both temperature dependent. So to measure the temperature dependence of one parameter, the

value of the other parameter has to be maintained constant. Let the volume be maintained constant at $V = V'$. The pressure has values P_1, P_2 and P_3 at empirical temperatures θ_1, θ_2 and θ_3 respectively. So here 'P' is chosen as the thermometric property. Hence when 'A' is in thermal equilibrium with 'C' the temperature of 'C' measured by this thermometer 'A' can be expressed as a function of 'P'

$$\theta(P) = \phi_1(P)_{V=\text{constant}} \dots\dots\dots (2.9)$$

Such a thermometer is called a **constant volume gas thermometer**. The same system 'A' would constitute a different kind of thermometer if the pressure is held constant and volume 'V' is chosen as the thermometric property. The same temperature is expressed as a function of volume.

$$\theta(V) = \phi_1(V)_{P=\text{constant}} \dots\dots\dots (2.10)$$

Such a thermometer is called a **constant pressure gas thermometer**. The forms of the functions ϕ_1 and ϕ_1 determine the temperature scales.

In place of gas any other thermodynamic system may be chosen as the thermometric substance provided it has a readily measurable property whose variation with temperature is smooth and significantly large. The other thermodynamic properties are held constant. The table below shows some common thermometers with the corresponding thermometric substances and thermometric properties.

Table 2.1

Thermometric substance	Thermometric property	Thermometer
Gas	Pressure(P)	Constant volume gas thermometer
Gas	Volume(V)	Constant pressure gas thermometer
Liquid column	Length(L)	Liquid thermometer
Pure metal	Electrical resistance(R)	Resistance thermometer
Two dissimilar metals joined in form of a loop	Thermo emf	Thermocouple thermometer
Black body radiation	Emissive power at given wavelength(e_λ)	Radiation Pyrometer
Paramagnetic salt	Magnetic susceptibility(χ)	Susceptibility thermometer
Semiconductor	Electrical resistance or electrical conductance	Semiconductor thermometer.

Let $X \rightarrow$ Any thermometric property of a thermometric substance 'A'

And $Y \rightarrow$ All other parameters of 'A' except temperature.

Y is maintained constant. Then the temperature measured by 'A' is a function of its thermodynamic property 'X'

$$\theta(X) = f(X)_{Y=\text{constant}} \dots\dots\dots(2.11)$$

The function 'f' in equation (2.11) is arbitrarily chosen to be a linear function of 'X'

So $\theta(X) = (aX)_Y \dots\dots\dots(2.12)$

Where 'a' is a constant and θ is the empirical temperature of the thermometer 'A' and of all systems in thermal equilibrium with 'A'.

Let $X_1 \rightarrow$ Measured value of the thermodynamic property when 'A' is in equilibrium with an arbitrary system 'B'

And $X_2 \rightarrow$ Measured value of the thermodynamic property when 'A' is in equilibrium with an arbitrary system 'C'

Then from equation (2.12) the ratio of the temperature of 'B' and 'C' are:

$$\frac{\theta_B(X_1)}{\theta_C(X_2)} = \frac{X_1}{X_2} \dots\dots\dots(2.13)$$

Step ii: a) To choose some standard state of the chosen system called fixed point.

b) To choose a numerical value to denote the temperature of of the fixed point

Both choices are arbitrary. The most popular choice of fixed point is the **triple point of water, where all three phases, ice, liquid water and water vapour coexist in equilibrium at an unique temperature and pressure. The temperature of triple point of water was arbitrarily assigned the value 273.16 degrees Kelvin denoted by 273.16K.** This is the fundamental fixed point of thermometry.

Then $\frac{\theta(X)}{\theta(X_{tr})} = \frac{X}{X_{tr}} \dots\dots\dots(2.14)$

Where $X_{tr} \rightarrow$ Measured value of the thermometric property at the triple point of water

$\theta(X_{tr}) = 273.16K$, the temperature at triple point of water.

$\theta(X) \rightarrow$ The temperature at which the value of the thermometric property is 'X'

Or $\theta(X) = 273.16K \cdot \left(\frac{X}{X_{tr}}\right) \dots\dots\dots(2.15)$

Now, if we substitute different thermometric properties mentioned in table 2.1 for 'X' we obtain one and the same temperature as:

$$\theta(P) = 273.16K \cdot \left(\frac{P}{P_{tr}}\right) \dots\dots\dots(2.16) \quad \text{on a constant volume gas thermometer}$$

$$\theta(R) = 273.16K \cdot \left(\frac{R}{R_{tr}}\right) \dots\dots\dots(2.17) \quad \text{on a resistance thermometer}$$

However it has been found that the readings $\theta(X)$, recorded by different thermometers with different thermometric properties 'X' differ from each other. This arises from the arbitrary choice of a linear relation between $\theta(X)$ and 'X'. The actual functional form depends on the thermometric substance chosen and the corresponding thermometric property 'X'. For example pressure of an ideal gas : $P = P_0\left(1 + \frac{1}{273}\theta\right) \dots\dots\dots(2.18)$ a linear relation.

$$\text{Thermo e.m.f. } e = \alpha\theta + \beta\theta^2 \dots\dots\dots(2.19) \quad \text{a non linear relation}$$

The equations (2.15), (2.16) and (2.17) show that only at triple, all the thermometers will show matching result as $\frac{X}{X_{tr}}$ will be = 1 in that case, while at all other temperatures they will disagree. In other words, each kind of thermometer has its own temperature scale. So to get matching result for all thermometers, any one kind of thermometer is taken as standard and all others are calibrated in terms of the standard one.

The ideal gas scale:

In the attempt to formulate a general scale of empirical temperature it was discovered that in case of constant volume gas thermometers, the readings were different when different gases were used. It was also found that the disagreement of readings with different gases decreased remarkably as the pressure of the gas at triple point of water was reduced. Real gases approach a common ideal behavior at very low pressure.

Let the bulb of a gas thermometer be filled with hydrogen gas and placed in steam condensing at standard pressure. If 'P_{S1}' be the final standard pressure of gas, the corresponding temperature $\theta(P_{S1})$ is given by:

$$\theta(P_{S1}) = 273.16\left(\frac{P_{S1}}{P_{tr}}\right)_V \dots\dots\dots(2.20)$$

Then some of the hydrogen gas is removed so as to decrease the gas pressure and the new value of pressure P_{S2} and the corresponding temperature $\theta(P_{S2})$ is calculated. This process is repeated several times by continuing to decrease the mass of hydrogen in the bulb so as to reduce the initial pressure P_{tr} stepwise, each time finding P_{Si} and corresponding $\theta(P_{Si})$. The

results for different steps are plotted on a $\theta(P_{Si})$ vs P_{tri} graph. The whole process is repeated by replacing hydrogen with several other gases and plotted on the same graph with same choice of scale.

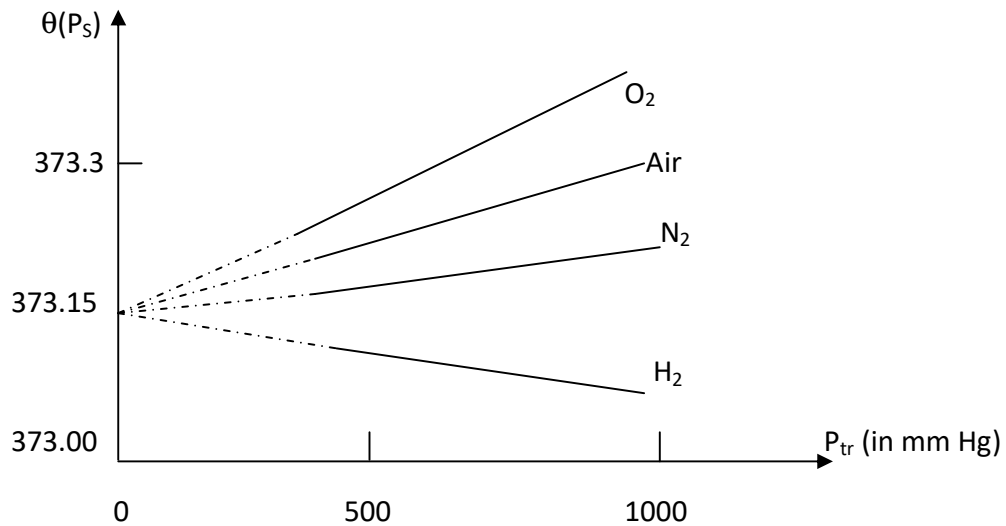


Fig. 2.4 Readings of a constant volume gas thermometer at the steam point using various gases at various initial pressures.

The plots for various gases, when extrapolated to $P_{tr} = 0$ intersect at the same point on the vertical axis at $\theta(P_S) = 373.15K$. This is the temperature of the steam point on a scale known as **ideal gas scale**. The ideal gas temperature scale is thus defined by the equation:

$$\theta = 273.16K \lim_{P_{tr} \rightarrow 0} \left(\frac{P}{P_{tr}} \right)_V \dots\dots\dots(2.21)$$

This scale is independent of the properties of any particular gas but depends only on the properties of ideal gas. The ice point (melting point of ice at standard pressure) temperature on this scale is 273.15K showing that in the ideal gas scale the temperature difference between ice point and steam point is exactly 100K. But the temperature 0K or absolute zero could not be defined in terms of ideal gas behavior.