

$\lim_{T \rightarrow 0} S = 0$, which completes the proof.

4.10: Joule-Thomson effect by cooling. Various gases can be liquefied with the help of Joule-Thomson effect by cooling. Here are various methods to liquefy some gases.

4.10.1: Liquefaction of Chlorine: The apparatus used for liquefaction of chlorine is shown in fig. (4.6).

The apparatus consists of a glass tube one end of which contains chlorine hydrate. Both ends of glass tube are closed. On heating the end containing chlorine hydrate, chlorine is evolved and a high pressure is developed. The other end of tube is immersed in a freezing mixture. When cooling is caused by freezing mixture, it is liquefied.

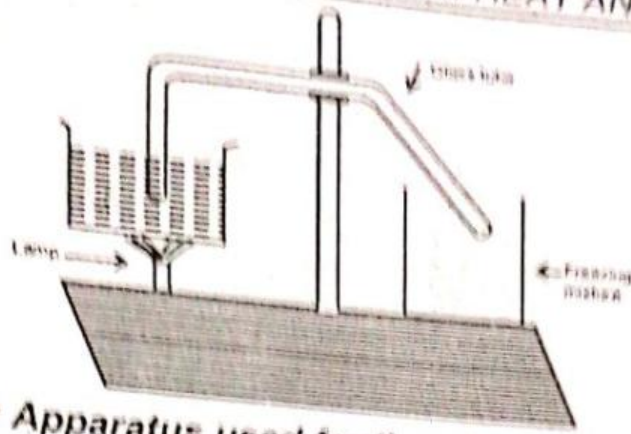


Fig. 4.6: Apparatus used for liquefaction of chlorine

4.10.2: Liquefaction of air:

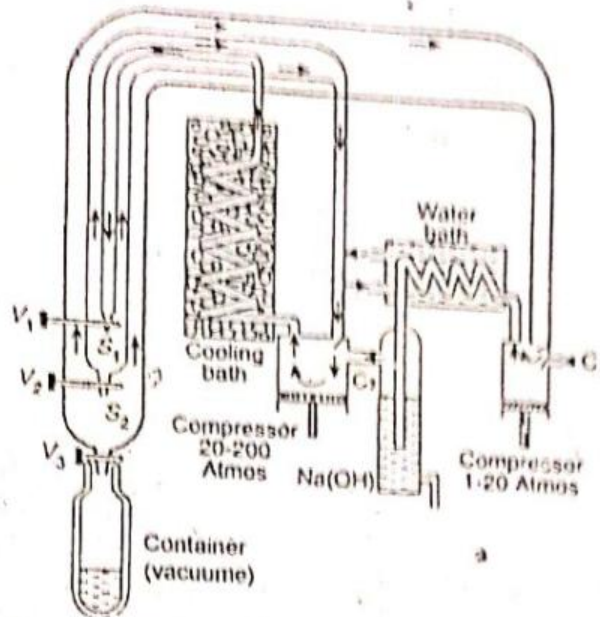


Fig. 4.7: Apparatus used for liquefaction of air

Air was liquefied by Linde with the help of Joule-Thomson effect. The schematic arrangement of apparatus is shown in fig. (4.7). C_1 and C_2 are two compressors. C_1 compresses incoming air to 10 atm pressure and this compressed air is cooled by passing through bath containing water. It is then led through a caustic soda bath to free from CO_2 . The gas then enters the compressor C_2 which compresses it to 200 atm pressure. The compressed air is then passed through a cooling bath and this cooled air is passed through inner pipe to suffer Joule-Thomson expansion at value V_1 . The cooled air is then made to flow through outer tube cooling the air flowing through inner pipe and finally returning to compressor C_2 where it is again compressed to 200 atm. After a few circulations, the incoming gas is cooled to a sufficiently low temperature and second valve V_2 is opened. The air is allowed to expand to 1 atm when it becomes liquid and is collected in a container through valve V_3 .

4.10.3: Liquefaction of Helium:

In 1908, Onnes liquefied helium and in 1926 Keesum obtained solid helium.

The apparatus used for liquefaction of helium is shown in fig. (4.8). He at pressure of 36 atm is passed through spirals S_1, S_2, S_3 out of which S_2 is immersed in boiling hydrogen. This cooled He below 17k is passed through porous plug for Joule-Thomson expansion and He cools down further. This He circulates round spiral and temperature goes on falling till it liquefies.

It has been found experimentally that at a temperature of 4.2 k and at 140 atm the helium solidifies.

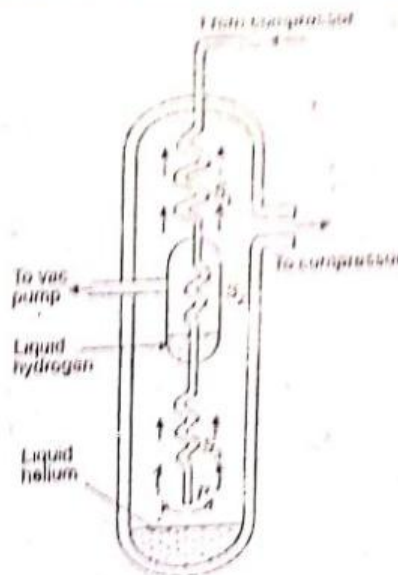


Fig. (4.8): Liquefaction of helium

MORE SOLVED EXAMPLES

Example 4.7: Prove that for Van der Waal gas $C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p$

Proof: We know that

$$S = S(v, T)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_v dT + \left(\frac{\partial S}{\partial v} \right)_T dv$$

$$\Rightarrow \frac{dS}{dT} = \left(\frac{\partial S}{\partial T} \right)_v + \left(\frac{\partial S}{\partial v} \right)_T \frac{dv}{dT}$$

$$\text{or } \left(\frac{ds}{dT} \right)_p = \left(\frac{\partial S}{\partial T} \right)_v + \left(\frac{\partial S}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p$$

$$\text{Now } C_p = \left(\frac{dQ}{dT} \right)_p = (T dS / dT)_p$$

$$C_p = T \left(\frac{dS}{dT} \right)_p$$

$$\Rightarrow C_p = T \left(\frac{\partial S}{\partial T} \right)_v + T \left(\frac{\partial S}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p$$

$$\text{From Maxwell equation } \left(\frac{\partial S}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \text{ \& } T \left(\frac{\partial S}{\partial T} \right)_v = C_v$$

$$\text{So } C_p = C_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p$$

$$\Rightarrow C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p \text{ as required.}$$

i.e., for an ideal gas C_v is independent of volume at a given temperature.

4.4: Joule-Thomson effect: When a gas is passed through porous plug and is then allowed to expand adiabatically, it is found that most of gases show a cooling effect, but hydrogen gas shows a heating effect at ordinary temperature. This phenomenon is called Joule-Thomson effect.

When a gas is passed through a porous plug, in fact both heating and cooling effects are produced. At a particular temperature, both effects balance each other. This temperature is called "inversion temperature". If a gas is above its inversion temperature, it will show heating effect after passing through a porous plug because in this case heating effect is greater than cooling effect. But a gas below its inversion temperature shows cooling effect after passing through porous plug because in this case cooling effect is greater than heating effect.

Porous Plug Experiment:

In order to verify Joule-Thomson effect, an experiment was performed by Joule and Lord Kelvin in 1852. This is known as porous plug experiment.

In this experiment, a gas is compressed to about $4\frac{1}{2}$ atm pressure and passed through a copper spiral which is placed in a hot oil bath. The gas is heated to temperature of oil bath on passing through spiral. The gas then enters into porous plug. The plug contains cotton wools held between two discs pierced with many holes. The plug is enclosed in a hollow wooden box in form of a cylinder. The cylinder is further surrounded by cotton wools placed in a metallic vessel. In this way porous plug is completely insulated from surrounding. A thermometer is placed with its bulb just above the plug. The thermometer is enclosed in a glass tube. The plug may be supposed to consist of large number of narrow tubes placed in parallel. The gas after passing through the pores of plug expands adiabatically. The complete arrangement of the experiment is show in fig (4.1).

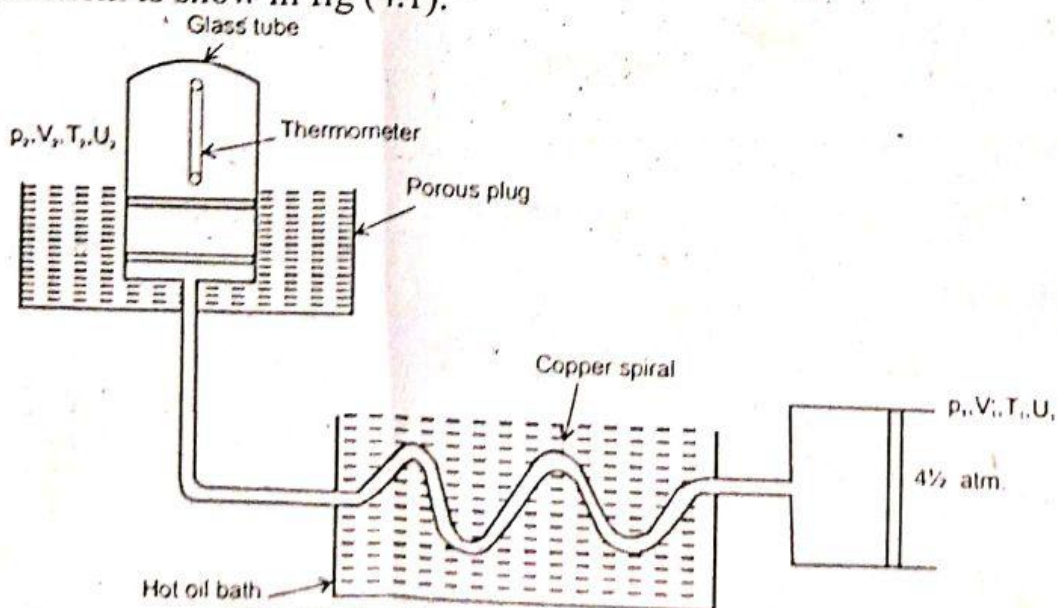


Fig (4.1): Porous plug experiment

The process in which a compressed gas expands adiabatically on passing through a porous plug or throttle is called throttling process.

Results: Following results were noted from this experiment:

- (1) Perfect gas shows neither heating nor cooling effect.
- (2) Almost all real gases show cooling effect.
- (3) Hydrogen gases shows heating effects.

Theoretical Explanation: Let p_1, V_1, T_1, U_1 be pressure, volume, temperature and internal energy of gas before passing through plug. Suppose these quantities become p_2, V_2, T_2, U_2 after throttling process.

$$\text{Work done on gas} = \int p dV = pV$$

$$\text{Net work done on gas} = p_1 V_1 - p_2 V_2$$

The process being adiabatic, this work appears as increase in internal energy of gas.

$$\text{So } p_1 V_1 - p_2 V_2 = U_2 - U_1$$

$$\Rightarrow p_1 V_1 + U_1 = p_2 V_2 + U_2$$

$$\Rightarrow pV + U = \text{constant}$$

$$\text{But } pV + U = \text{enthalpy of gas} = H$$

$$\Rightarrow H = \text{constant}$$

So we find that enthalpy of gas remains constant during throttling process.

The change in temperature with change in pressure keeping enthalpy constant is called Joule-Thomson co-efficient.

$$\mu = \left(\frac{\partial T}{\partial p} \right)_h$$

Where h is enthalpy per gram mole of gas and

$$h = u + pv$$

u is entropy per gram mole & v is volume per mole.

$$\text{Now } dh = du + pdv + vdp$$

$$\text{But } TdS = du + pdv$$

$$\text{So } dh = TdS + vdp \rightarrow (4.20)$$

From second TdS equation,

$$TdS = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp$$

Putting above value of TdS in (4:20),

$$dh = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp + vdp$$

$$\Rightarrow C_p dT = \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dp + dh$$

$$\Rightarrow dT = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dp + \frac{1}{C_p} dh \rightarrow (4.22)$$

This equation shows that

$$T = T(p, h)$$

$$\Rightarrow dT = \left(\frac{\partial T}{\partial p}\right)_h dp + \left(\frac{\partial T}{\partial h}\right)_p dh \rightarrow (4.23)$$

A term by term comparison of equations (4.22) and (4.23) shows that,

$$\left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{C_p} \left\{ T \left(\frac{\partial v}{\partial T}\right)_p - v \right\}$$

$$\Rightarrow \mu = \frac{1}{C_p} \left\{ T \left(\frac{\partial v}{\partial T}\right)_p - v \right\} \rightarrow (4.23)$$

For a perfect gas:

We have $pv = nRT$

$$\Rightarrow v = nRT/p, \quad \frac{\partial v}{\partial T} = \frac{nR}{p}$$

Putting in (4.23), we get,

$$\mu = \frac{1}{C_p} \left[T \cdot \frac{nR}{p} - \frac{nRT}{p} \right] = 0$$

i.e., Joule Thomson co-efficient for a perfect gas is zero. So perfect gas is neither heated nor cooled during throttling process.

For a real gas: From first and second laws of thermodynamics, we have,

$$TdS = du + pdv$$

Now, $d(pv) = pdv + vdp \Rightarrow pdv = d(pv) - vdp$.

$$\text{So } TdS = du + d(pv) - vdp$$

$$\Rightarrow T \frac{dS}{dp} = \frac{du}{dp} + \frac{d(pv)}{dp} - v$$

In terms of partial derivatives,

$$T \left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial u}{\partial p}\right)_T + \left(\frac{\partial(pv)}{\partial p}\right)_T - v$$

Using Maxwell equation,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

So above equation becomes,

$$T \left(\frac{\partial v}{\partial T}\right)_p - v = -\left(\frac{\partial u}{\partial p}\right)_T - \left(\frac{\partial(pv)}{\partial p}\right)_T$$

$$\Rightarrow \frac{1}{C_p} \left\{ T \left(\frac{\partial v}{\partial T}\right)_p - v \right\} = \frac{1}{C_p} \left\{ -\left(\frac{\partial u}{\partial p}\right)_T - \left(\frac{\partial(pv)}{\partial p}\right)_T \right\}$$

$$\Rightarrow \mu = -\frac{1}{C_p} \left(\frac{\partial u}{\partial p}\right)_T - \frac{1}{C_p} \left(\frac{\partial(pv)}{\partial p}\right)_T \rightarrow (4.23a)$$

First term measures deviation from Joule's law. For an ideal gas it is zero, but for real gas it is not zero. This happens due to intermolecular attraction between molecules of a gas. As $\left(\frac{\partial u}{\partial p}\right)_T$ is itself a negative quantity, the portion of internal energy which is due to intermolecular attraction always decreases with increase of pressure. Hence due to deviation from Joule's law, the Joule-Thomson effect is a cooling effect.

The second term on R.H.S of (4.23a) measures a deviation from Boyle's law. The compressibility curves drawn for pv versus p show that $\frac{\partial(pv)}{\partial p}$ has a negative value at low pressures so that this term contributes towards a cooling effect. For high pressures $\frac{\partial(pv)}{\partial p}$ has a positive value so that it contributes towards heating effect and in between at a particular temperature $\frac{\partial(pv)}{\partial p} = 0$. The second term may give rise to cooling, heating or zero effect.

Hence if the sum of these two terms is positive, there is a net cooling effect, if it is -ve, a net heating effect and if it is zero, there is neither a heating nor cooling effect.

For hydrogen gas it is found that value of pv decreases with decrease in pressure so second term of right side of above equation (4.23a) is negative which means a heating effect. This is numerically greater than cooling effect due to first term. So hydrogen gas shows a heating effect during throttling process. Same is the

$$T = \frac{eV}{k_B}, \mu = 0, \text{ no effect.}$$

4.6) **Thermo-electricity:** If rod of iron is welded to two pieces of copper wires X and Y and free ends of copper wires are connected to galvanometer, if one of the junctions is at high temperature than other, the galvanometer shows a deflection. This current is called thermoelectric current and this arrangement is known as thermocouple. In thermo-electricity we discuss three effects:

- (i) Seebeck effect.
- (ii) Peltier effect.
- (iii) Thomson effect.

Now we explain these effects one by one.

4.6.1: **Seebeck effect:** When two dissimilar metals are joined together so as to form a loop and one junction is heated while other junction is cold, then current starts flowing through the loop. The production of e.m.f by such a loop is known as Seebeck effect.

Suppose A and B are two metal strips joined at two ends. Let metal A has high concentration of free electrons than metal B. If both junctions are at same temperature, then contact potential difference produced at both junctions being equal and opposite will cancel each other and there is no net e.m.f in circuit. When one of junction is heated, the contact potential difference changes at hot junction and current starts flowing through the centre. The pair of metals used in form of loop is called thermocouple.

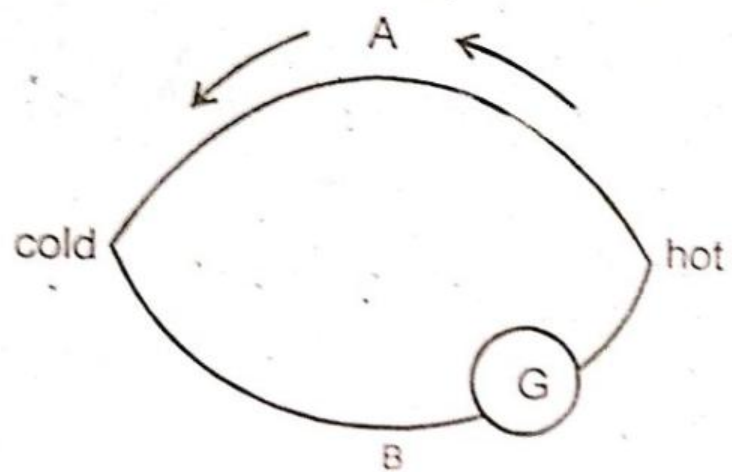


Fig. 4.2: Seebeck effect

The e.m.f generated depends upon pair of metals forming thermocouple and temperature difference between the two junctions. Experimentally it has been observed that for small temperature difference e.m.f is proportional to temperature. For large temperature difference e.m.f. increases and for a certain temperature of hot junction, it becomes maximum, this temperature is called neutral temperature. The neutral temperature is independent of temperature of cold junction & is constant for a given couple. If temperature of hot junction is further increased beyond the neutral temperature, the thermo e.m.f decreases. Variation of thermo e.m.f. with temperature is shown in fig. (4.3), which is a parabola.

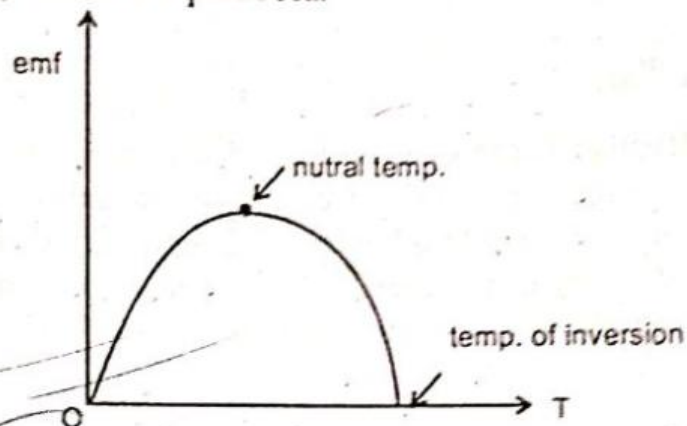


Fig. 4.3: Variation of e.m.f. with T

The temperature at which e.m.f. reduces to zero is called temperature of inversion.

4.6.2: Peltier Effect:

It is converse of Seebeck effect *i.e.*, when a current is passed through a thermocouple, one junction becomes heated and other junction cold. This effect is called Peltier effect.

Suppose we have Fe-Cu thermocouple. Junction A is at lower temperature than B. A battery is inserted in thermocouple to pass a current in direction as shown in fig. (4.4). When current passes through junction, hot junction becomes cold. This effect is explained as follows:

At junction A, Fe is at higher potential than Cu, so current flows from A to B and energy is liberated in form of heat at this junction. At junction B current flows from lower potential to higher potential and so require extra energy which is absorbed from junction in form of heat, so junction B becomes cold. This effect is reversible which means that if we change direction of e.m.f., the junction A will become cold and B will become hot.

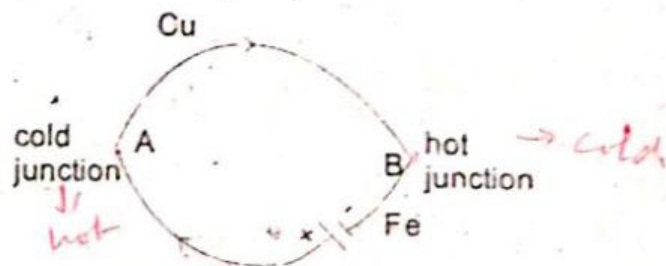


Fig. 4.4: Peltier effect

The amount of heat energy absorbed or evolved per unit time when a unit current is passed through a junction is called Peltier co-efficient.

If a current I is passed for a time t , the energy absorbed or evolved at junction is,

$$E = \pi It, \quad \pi \text{ is Peltier co-efficient.}$$

If V is contact potential difference, the energy absorbed or evolved at junction can also be written as,

$$E = VIt$$

$$\text{So } \pi It = VIt$$

$$\Rightarrow \pi = V.$$

i.e., Peltier co-efficient is numerically equal to contact potential difference at junction.

4.6.3: Thomson effect: If a current is passed in an unequally heated wire, heat is evolved or absorbed. This phenomenon is called Thomson effect.

In certain substances like Cu and Ag etc., heat energy is absorbed when current flows from a point at lower temperature to a point at higher temperature and heat is evolved when current flows from a point at higher temperature to a point at lower temperature. Thomson effect for such substances is said to be positive.

In some substances like Fe, Co etc., heat energy is evolved when current flows from a point at lower temperature to a point at higher temperature. Thomson effect is said to be negative for these metals.

In an unequally heated wire kinetic energy of free electrons is different at different points. So free electrons have a tendency to move from one point to another. Therefore, a contact potential difference will be produced in same metal depending upon temperature difference. If current is passed from a higher potential to a lower potential, energy will liberated in form of heat. But if current is passed from a lower potential to higher potential, energy will be absorbed.

The amount of energy absorbed or evolved by passing unit current in unit time through 1°C temperature difference is called Thomson co-efficient.

If there are two points at a temperature difference of 1°C and a current I is passed for a time t , heat absorbed or evolved is,

$$E = \sigma It$$

If V is contact potential difference, then

$$E = VIt$$

$$\Rightarrow \sigma It = VIt$$

$$\Rightarrow \sigma = V$$

i.e., Thomson co-efficient is numerically equal to contact potential difference.

4.6.4: Total e.m.f in a thermocouple:

Consider a Fe-Cu thermocouple with two junctions at temperatures T_1 and T_2 where $T_2 > T_1$. Due to this difference of temperature between junctions an e.m.f. will be produced which passes a current from Fe to Cu at junction at A and from Cu to Fe at junction B.

At junction A current flows from Fe to Cu *i.e.*, from higher potential to lower potential. So π_1 heat is evolved for a unit quantity of current. The current passes in Cu from lower to higher temperature so heat will be absorbed due to Thomson effect. The amount of heat absorbed for unit current is,

$$\int_{T_1}^{T_2} \sigma_A dt$$

At junction B current flows from Cu to Fe *i.e.*, from lower potential to higher potential, π_2 heat will be absorbed. In Fe, current flows from a higher temperature to lower temperature, so $-\int_{T_1}^{T_2} \sigma_B dt$ heat will be absorbed due to Thomson effect, where

σ_B is Thomson co-efficient for Fe. Amount of heat absorbed will be equal to total e.m.f in circuit.

$$\begin{aligned} U &= \pi_2 - \pi_1 + \int_{T_1}^{T_2} \sigma_A dt - \int_{T_1}^{T_2} \sigma_B dt \\ &= (\pi_2 - \pi_1) + \int_{T_1}^{T_2} (\sigma_A - \sigma_B) dt. \end{aligned}$$

For small temperature difference *i.e.* when $T_1 = T$ and $T_2 = T + dT$, above equation becomes,

$$\begin{aligned} U &= d\pi + (\sigma_A - \sigma_B) dt \\ \Rightarrow \frac{dU}{dt} &= \frac{d\pi}{dt} + (\sigma_A - \sigma_B) \end{aligned}$$

$$\Rightarrow \text{Thermoelectric power} = \frac{d\pi}{dt} + (\sigma_A - \sigma_B) \quad \rightarrow (4.26)$$

4.7: Production of low temperatures:

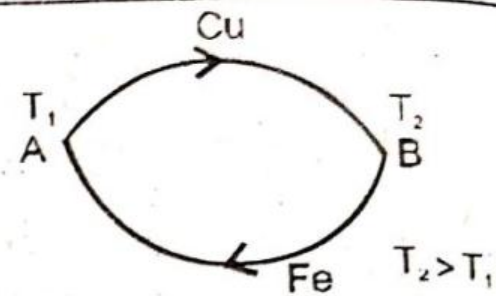


Fig. 4.5: A thermocouple