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Semester-II**

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**Lesson: Magnetic work and adiabatic cooling**

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# Magnetic work and adiabatic cooling

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## Objectives

By reading this lesson, you will be able to understand;

- ✓ Different forms of works in thermodynamics
- ✓ The phenomenon of magnetization and demagnetization
- ✓ How adiabatic demagnetization leads to cooling effect?
- ✓ How ultra low temperatures could be achieved?
- ✓ The significance of magnetic cooling.

## 12.1 Introduction

The materials are basically divided into three general categories *vis.* diamagnetic, paramagnetic, and ferromagnetic owing to their magnetic properties. By magnetic properties, we are concerned here with the microscopic properties *i.e.* arrangement of atomic/molecular magnetic dipole moments in the presence/absence of external magnetic field. The diamagnetic materials possess negative magnetic **susceptibility**( $\chi$ ) and the **induced** magnetic dipoles align in opposite direction to that of external magnetic field. The magnetic susceptibility of these materials is found to be temperature independent. The ferromagnetic substances, on the other hand, possess positive and larger values of  $\chi$  due to exchange interactions between their atomic/molecular magnetic dipoles. They possess non-zero spontaneous magnetization even in the absence of external magnetic field. The alignment of the tiny dipoles in such materials strongly depends on the temperature of the specimen. Increase in the temperature causes the randomization of these tiny dipoles which in turn reduces the magnetization value and at a certain temperature  $T_c$  (different for different ferromagnetic substance), the specimen becomes paramagnetic. The paramagnetic phase of the specimen is characterized by smaller positive values of  $\chi$  ( $\ll 1$ ) *i.e.* a relatively strong magnetic field is required to align (in the direction of field) the dipoles.

We have not mentioned the effect of temperature on the alignment of atomic/molecular magnetic dipoles for different specimens. Since the susceptibility of para and ferromagnetic materials possess strong temperature dependence, the temperature plays very significant role in the orientation of these tiny dipoles. For a paramagnetic specimen, the tiny dipoles may be aligned uniformly in the applied field direction at lower temperatures. However, at higher temperatures, the dipoles point in random directions because the thermal energy ( $k_B T$ ) is much larger than the magnetic energy irrespective of applied magnetic field. Interestingly, the temperature dependence of alignment of paramagnetic dipole moments could be utilized to cool the specimen to ultra low temperatures and method of the same is discussed in this lesson. However, as the phenomenon is related with the concept of magnetic work, let us revisit briefly the concept of works in thermodynamics.

## 12.2 Works in thermodynamics

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While studying the first law of thermodynamics, we found that the transfer of heat from a system to another results in the change of the total energy stored in the system and a fraction (or total), depending up on the process, of this energy may be used in the form of work. The work, in this way, performed by (or on) the system is measurable solely from knowledge of external macroscopic constraint variables which always occur in conjugate pairs. The examples of such variables are pressure and volume, mole fraction and chemical potential, and magnetic flux density and magnetization *etc.* In a broad sense, work in thermodynamics may be classified into two categories: Mechanical and Non-mechanical work. The work performed by actions such as compression, stirring, and rubbing *etc.*, for example works done due to the change of volume against a resisting pressure, come under the category of mechanical work. Whereas, the gravitational field may change the spatial distribution of the matter within the system and the work performed will be of non-mechanical kind. Let us discuss briefly about Mechanical and Non-mechanical works in thermodynamics:

### 12.2.1 Pressure-volume work

We have been familiarized with pressure-volume work during the discussion of first law of thermodynamics. The heat supplied to a container having gas molecules with a piston at constant pressure (isobaric process) causes the expansion of the gas *i.e.* gas molecules perform work against pressure. If the value of pressure and change in the volume of the gas be  $p$  and  $dV$  respectively, then the work ( $dW$ ) done by the gas may be obtained as;

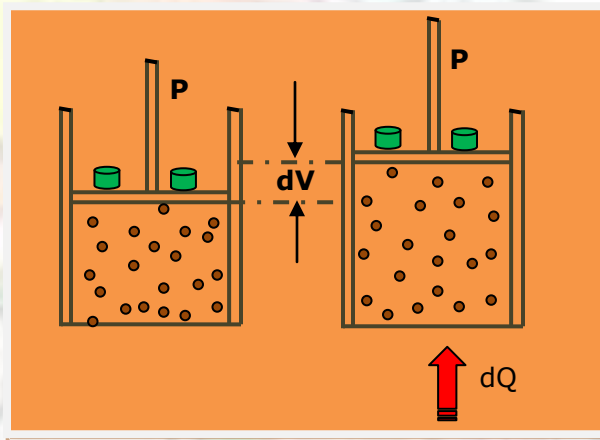


Figure 12.1: Cartoon illustrating pressure-volume work

$$dW = p dV$$

It is worth to mention here that above process took place at constant temperature (isothermal process) and hence the total heat provided to the gas molecules is converted into work. Similarly, if the volume of gas changes from its initial volume  $V_i$  to some final value  $V_f$ , then the total work done by the gas may be obtained as;

$$W = \int_i^f p dV$$

$$\text{or } W = \int_i^f \frac{nRT}{V} dV \quad (\text{as } pV = nRT)$$

$$\text{or } W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln \frac{V_f}{V_i} \quad (12.2)$$

On the other hand, it is easy to understand that the work done during an isochoric process is zero because the volume remains the same (*i.e.*  $dV = 0$  and hence  $W = 0$ ).

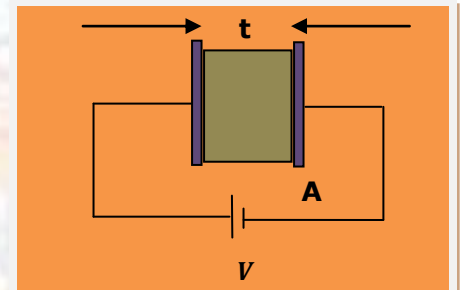
## 12.2.2 Non-Mechanical forms of work

Non-mechanical forms of work in thermodynamics come into the picture due to establishment of the long range force fields present in the surroundings *i.e.* outside of the system, of thermodynamic systems, but their fields may penetrate into the system. These long range forces are different from those thermodynamic forces originates due to any non-equilibrium condition of the system. These long-range forces are forces in the ordinary physical sense of the word *e.g.* gravitational, electrical, and magnetic forces *etc.* Let us discuss how some of these forces contribute to work.

### 12.2.2.1 Work due to electrical polarization of a dielectric solid

Consider a slab of isotropic dielectric material having thickness  $d$  and area  $A$  is placed between the two plates of a parallel plate capacitor connected with a battery of emf  $V$  as shown in the figure. The potential difference on the plates will set up almost uniform electric field between the plates which may be written as;

$$E = \frac{V}{t} \quad (12.3)$$



**Figure 12.2:** Charging of a parallel plate capacitor

Moreover, during the charging of the capacitor, the work is to be done by the battery. If the work done in changing the charge on the capacitor by an infinitesimal amount  $dq$  be  $dW$ , then we may have;

$$\begin{aligned} dW &= dq V \\ \text{or } dW &= Etdq \end{aligned} \quad (12.4)$$

The charge  $q$  may be expressed in terms of the electric displacement vector ( $D$ ) as;

$$\begin{aligned} q &= DA \\ \text{or } dq &= d(DA) \\ \text{or } dq &= Ad(D) \end{aligned} \quad (12.5)$$

But, with the expression  $D = \epsilon_0 E + P$ , where  $P$  is the polarization per unit volume, we may write equation (12.5) as;

$$\begin{aligned} dq &= Ad(\epsilon_0 E + P) \\ \text{or } dq &= Ad(\epsilon_0 E + P) \\ \text{or } dq &= Ad \left( \epsilon_0 E + \frac{P_{Total}}{v} \right), \text{ where } v \text{ is volume of the dielectric material} \end{aligned}$$

With this value of  $dq$ , the work done may be obtained as;

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$$dW = Etdq = Et \left[ Ad \left( \epsilon_0 E + \frac{P_{Total}}{v} \right) \right]$$

$$\text{or } dW = \epsilon_0 EAtdE + \frac{EAtd}{v} dP_{Total}$$

$$\text{or } dW = v\epsilon_0 EdE + EdP_{Total} \quad (12.6)$$

In equation (12.6), the first term represents the work required to increase the electric field by an amount  $dE$  and will be present even in the absence of the dielectric (*i.e.* in vacuum too). The second term gives the work needed to change the net polarization of the dielectric by  $dP_{Total}$  and will be zero in absence of dielectric. As we are concerned here with only the work required for changing the polarization and hence, the work done on the dielectric is;

$$dW = EdP_{Total} \quad (12.7)$$

It is to be mentioned here that above result is general for any isotropic dielectric material in uniform electric field irrespective of the specifications such as parallel plate of any other types of capacitors. With the help of above expression, the total work in changing the polarization of a dielectric from some initial value  $P_i$  to some final one  $P_f$  can be obtained by integration;

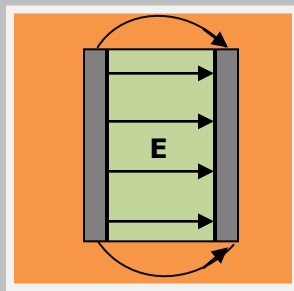
$$W = \int_{P_i}^{P_f} EdP_{Total} \quad (12.8)$$

The expressions for the other non-mechanical forms of work may be obtained in a similar way and such discussions have already been made in previous lessons. Here we will be focusing more on magnetic work and related phenomenon. As discussed briefly in the introduction of this chapter, let us discuss first about magnetization and demagnetization.

### Did you know?

**Anisotropic dielectrics:** The dielectrics which response (to the applied electric field) differently along different directions.

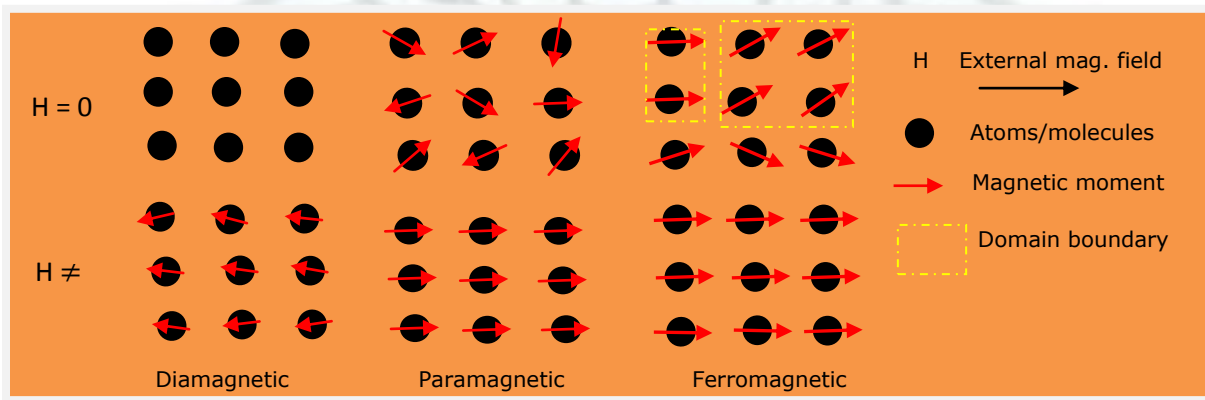
**Fringing effect:** In a parallel plate capacitor, the electric field does not end abruptly at the edge of the plates. Some field lines exist outside the plates that curve from one to the other and the presence of such curved field lines is termed as fringing effect. Due to the fringing phenomenon, the value real capacitance is larger than what we calculate using the ideal formula.



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## 12.3 Magnetization

We know that all the materials possess less or more magnetic character, depending upon which category *vis. dia, para, and ferromagnetic etc* they belong. The magnetic properties of materials are mainly due to the orbital and spin motion of the electrons in the atoms. Being a charge particle, its spin/round motion constitutes a tiny current and we exercised the fact that current loop may be treated as a tiny magnetic dipole. In the absence of external magnetic stimuli these tiny magnetic dipoles are directed in random directions due to thermal energy and the net magnetic dipole moment of the material comes out to zero. We know a magnetic dipole experiences a torque when placed in an external magnetic field. The torque tries to align the magnetic dipole in the direction of applied magnetic field.



**Figure 12.3:** Cartoon showing the orientation of atomic magnetic dipoles in the absence/presence of external magnetic field in dia, para, and ferromagnetic samples.

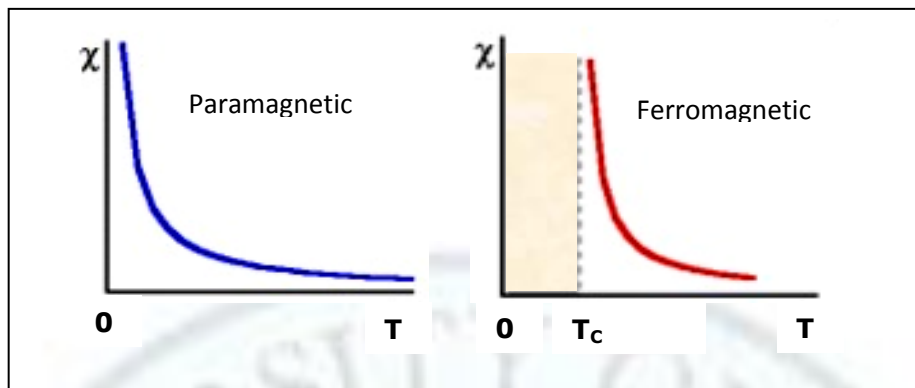
When a piece of some magnetic material is placed in external magnetic field, the tiny dipoles present (induced) in the material get aligned in the (or opposite) direction of applied field (shown above). The order of their alignment depends on the strength of applied field, temperature and the nature of material itself. The phenomenon of the alignment of magnetic dipoles in external magnetic field is termed as **Magnetization ( $M$ )**. Mathematically, it is defined as the magnetic dipole moment per unit volume of the specimen. Experimentally, the magnetization is directly proportional to the applied magnetic field ( $H$ ) *i.e.*

$$M \propto H$$

or  $M = \chi_m H$  (12.9)

where  $\chi_m$  is the magnetic susceptibility of the material. As discussed, magnetization and hence  $\chi_m$  strongly depends on the temperature, below are given some plots showing the variation of  $\chi_m$  with temperature (note that  $\chi_m$  for diamagnetic materials is temperature independent).

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**Figure 12.4:** Variation of magnetic susceptibility in para, and ferromagnetic materials with temperature.

In above figure,  $T$  and  $T_c$  are temperature and transition temperature respectively. To have an idea about the magnitudes of  $\chi_m$ , below is given the range of susceptibilities of different materials;

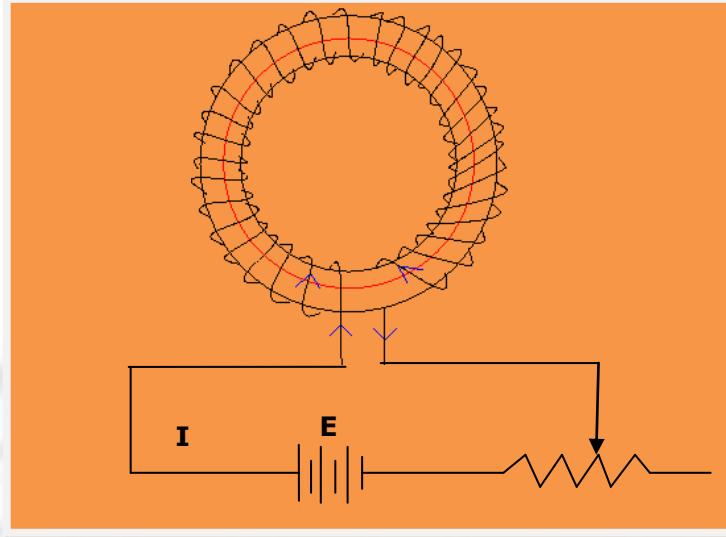
S. No.	Type of the substances	Volume susceptibility (order of magnitude)	Examples
1	Diamagnetic	$\sim 10^{-5}$ ( $<0$ )	Water, carbon, silver, bismuth etc.
2	Paramagnetic	$10^{-3}$ to $10^{-5}$ ( $>0$ )	Sodium, magnesium, lithium etc.
3	Ferromagnetic	Very high values up to $\sim 10^6$	Iron, cobalt, nickel etc.

### 12.4 Magnetic work

As discussed in section 12.3, to align the tiny magnetic dipoles, we require external magnetic field. In the process of magnetization, some work has to be done by the applied magnetic field. To obtain the expression for such magnetic work, let us consider a sample of paramagnetic substance in the form of a ring having cross sectional area and the mean circumference as  $A$  and  $C$  respectively. To get magnetic field around the ring, an insulated conducting wire is wound around the ring in the form of a **toroid** with say  $N$  closely spaced turns. The ends of the wire are connected with a battery and a variable resistor as shown below;



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**Figure 12.5:** Cartoon showing the experimental set up for changing the magnetization of a paramagnetic solid in the form of a ring.

A dc current through the winding wire sets up a magnetic induction  $B$  that will nearly be uniform over the cross-section of the toroid. The atomic magnetic dipoles experience torque due this induction field  $B$  and will align themselves in the direction of the field. Suppose, the current in the circuit is changed which in turn changed the magnetic induction by an amount  $dB$  in time  $dt$ . According to Faraday's law of electromagnetic induction, this change in magnetic induction will induce in the windings a back emf say ( $E$ ), where;

$$E = -NA \frac{dB}{dt}$$

Now, if during the time interval  $dt$ , charge  $dq$  moves in the circuit. Then the work done by the battery to maintain the current will be given as;

$$dW = -Edq$$

$$\text{or } dW = NA \frac{dB}{dt} dq$$

$$\text{or } dW = NA \frac{dq}{dt} dB$$

$$\text{or } dW = NAI dB \quad (12.10)$$

The magnetic field intensity  $H$  inside a toroidal winding having current  $I$  is given by;

$$H = \frac{NI}{L}$$

$$\text{Or } H = \frac{NAI}{AL}$$

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$$\text{Or } H = \frac{NAI}{V}$$

where  $V = AL$  is the volume of paramagnetic material. Therefore,  $NAI = VH$ , and hence the work done will be:

$$dW = VHdB$$

Now, with the definition of magnetic induction vector;

$$B = \mu_0 \left( H + \frac{M_T}{V} \right)$$

where,  $\mu_0$  is the magnetic permeability of the free space, and  $M_T$  is the total magnetization of the specimen. From above relation, we may express  $dW$  as;

$$dW = VHd \left[ \mu_0 \left( H + \frac{M_T}{V} \right) \right]$$

or  $dW = VHd(\mu_0 H) + \mu_0 HdM_T$  (12.11)

First term on the RHS of above relation represents the work required to increase the magnetic field in a volume  $V$  of free space by an amount  $d(\mu_0 H)$  and the second term is the work needed to increase the total magnetization of the material by an amount  $dM_T$ . As we are concerned here with the work done on/by a paramagnetic specimen that will be given by;

$$dW = \mu_0 HdM_T \quad (12.12)$$

Now, the total work done in changing the total magnetization from  $M_{T_i}$  to  $M_{T_f}$  may be obtained by integration i.e.

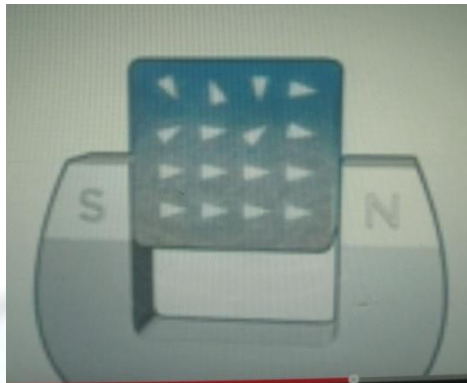
$$W = \mu_0 \int_{M_{T_i}}^{M_{T_f}} HdM_T \quad (12.13)$$

### 12.5 Adiabatic demagnetization

We know that the atomic/molecular magnetic dipoles of a substance are randomly oriented in the absence of any external magnetic field and get aligned in field direction if external field is applied. This phenomenon was named as magnetization of the substance. If the external field is switched off, these dipoles restore their original random distribution to ensure zero magnetization (however, for some materials such as ferromagnetic, the dipoles do not return to their original distribution and retain some **residual magnetization**). This phenomenon is known as demagnetization and, if it occurs adiabatically, the atomic dipoles attain their original distribution in expense of their internal energy which results the drop in the temperature the substance. This fact has been potentially utilized to cool the paramagnetic salts to ultra low temperatures. The process heating/cooling of a paramagnetic substance due to magnetization/demagnetization is known as **magneto-caloric effect**. Below is given the snapshot of a video illustrating this effect. The video may be seen using the link: <http://youtu.be/xVhAvp17xJ8> (Credit to be given to BASF).

## Magnetic work and adiabatic cooling

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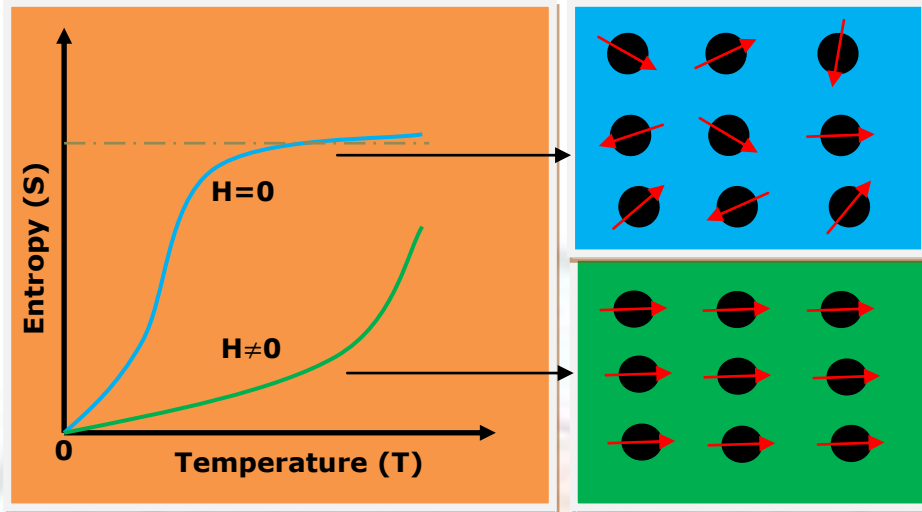
The possibility of producing ultra low temperatures by utilizing adiabatic demagnetization was theoretically suggested by Debye (1926) and Giauque (1927) independently. In 1931, Simon and Kurti, & Giauque and McDougall were succeeded to observe it experimentally.

### Did You Know?

- ✓ The ferromagnetic materials such as iron possess strong magnetization due to the exchange interaction between their atomic magnetic dipoles. Groups of a large number of atomic dipoles having same dipolar orientations are formed which are known as domains.
- ✓ These materials once magnetized, retain remarkable residual magnetization even when the magnetizing field is switched off.
- ✓ Can you suggest some other methods of demagnetization? You may visit the link to get answer.  
<http://youtu.be/CU3pG7PWzfs>

The process of cooling by adiabatic demagnetization can easily be understood by taking into account the concept of entropy. We know, entropy is the measure of disorder of the system concerned and is directly related with temperature. Higher the temperature, higher will be the randomization and hence the entropy of the system. In a paramagnetic substance there are number of things that contributes to its entropy at normal temperatures. The contributions such as thermal motion of ions present at lattice sites, motion of free electrons, and ionic dipoles (if any) are dominant at higher temperatures. However, at lower temperatures (say at liquid helium temperature), the above contributions becomes negligible and hence may be ignored. At lower temperatures, the contribution due to atomic magnetic dipoles of the paramagnetic substance becomes significant and the entropy of the system may be assumed only due to the same. As we know, in the absence of external magnetic field, the orientation of atomic magnetic dipoles is random and hence the higher entropy of the substance. However, these magnetic dipoles get aligned in the field direction in the presence of sufficient external magnetic field. This increases the ordering and hence entropy lowers. To give you an idea, below is shown a plot between entropy and temperature of a paramagnetic substance in absence/presence of external magnetic field.

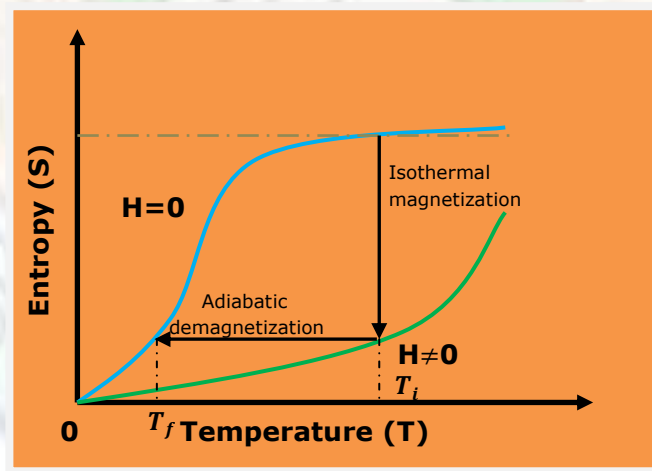
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**Figure 12.6:** Variation of magnetic entropy with temperature of paramagnetic substance in absence/presence of external magnetic field.

The process of cooling of the paramagnetic substance involves two steps:

- 1. Isothermal magnetization:** At first, the external magnetic field across the paramagnetic specimen, kept at liquid helium temperature ( $\sim 1.2-1.5$  °K), is increased isothermally. This forces the atomic magnetic dipoles to align in the field direction which lowers the entropy of the specimen to lower value [Fig. 12.7].



**Figure 12.7:** T-S plot of paramagnetic specimen showing different steps to obtain cooling.

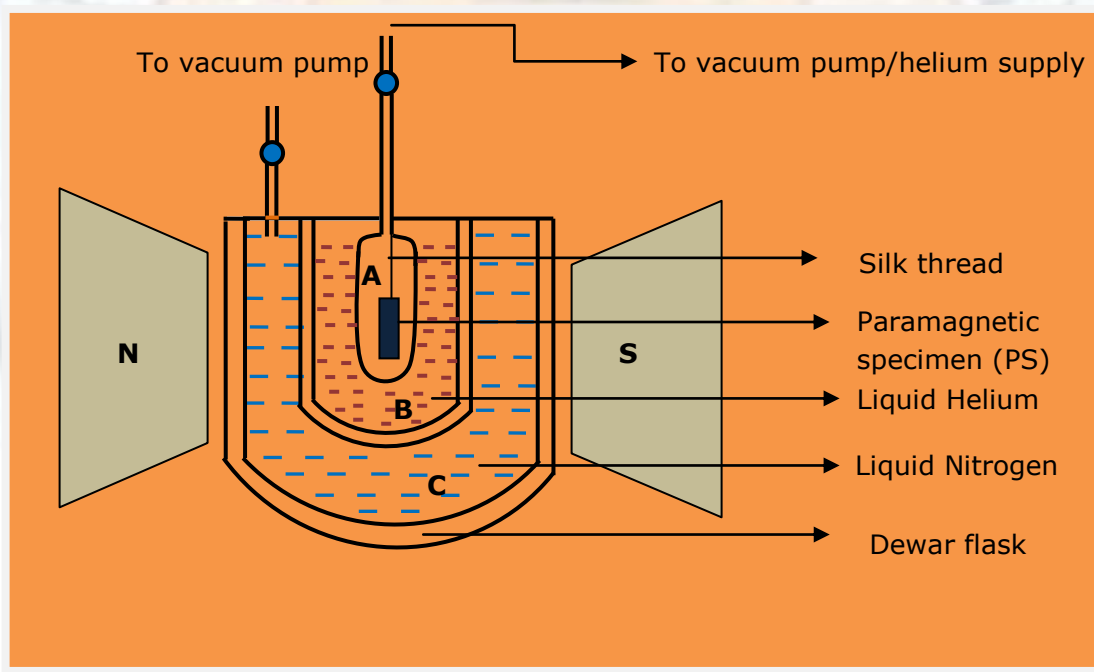
- 2. Adiabatic demagnetization:** This is the second step in which the magnitude of external magnetic field is reduced slowly adiabatically. In the absence of external field, the magnetic dipoles acquire their original random distribution. However, since the process is performed adiabatically, the magnetic dipoles lose some of their internal energy and hence the temperature of the specimen gets lowered [Fig. 12.7].

## Magnetic work and adiabatic cooling

Now let us discuss how the above steps are achieved experimentally. For that, the paramagnetic specimen (PS) is suspended inside a cylindrical tube (A) with the help of a silk thread. The tube A is surrounded by a liquid helium bath (B), kept in a **Dewar vessel**, under a reduced pressure ( $\sim 1\text{mm}$  of Hg). The helium gas may be entered or evacuated from tube A by using a pump. The liquid helium bath B is further surrounded by liquid nitrogen bath. To apply external magnetic field, the whole arrangement is placed between the poles of a strong electromagnet [Fig. 12.8].

The **working** of the adiabatic demagnetization may be understood as follows;

At first, the helium gas is entered in bulb A which makes the thermal contact of the PS with liquid helium in bulb B and as a result, the PS acquires the liquid helium temperature ( $1.2\text{--}1.5\text{ }^\circ\text{K}$ ). The electromagnet is then switched on producing magnetic field ( $\sim$  few tesla) which intensely magnetizes the PS and heat generated due to so is carried away by helium in bulb A to bulb B. The PS is now getting cooled and highly magnetized. Now, the PS is thermally isolated from B and C by pumping out the helium gas from bulb A. Switching off slowly the electromagnet results in the demagnetization of the PS adiabatically which lowers the temperature of PS.



**Figure 12.8:** Cartoon showing the set up for adiabatic cooling experiment

It is noticeable that the direct measurement of the temperature of the specimen attained after demagnetization is quite difficult. It is indirectly determined by measuring the magnetic susceptibility of the specimen at the beginning and end of the experiment and, for that, a coaxial solenoid coil is fitted around the bulb A. With the assumption that **Curie's law** holds at low temperatures and hence the relation  $\chi \propto \frac{1}{T}$ , the temperature of the PS is estimated.

### 12.6 Summary

- ✓ **Thermodynamic works** may be categorized into mechanical and non-mechanical forms.
- ✓ The work performed by actions such as compression, stirring, and rubbing *etc*, come under the category of **mechanical work**.
- ✓ The external fields such as gravitational, electrical *etc* could change the spatial distribution of the matter within the system and the work performed will be of **non-mechanical** kind.
- ✓ The work needed in changing the **polarization** of a dielectric material and is supplied by external source of emf. Such type of work is an example of non-mechanical form.
- ✓ The spin (about its own axis) and orbital motions (around the nucleus) of negatively charged electrons in atoms are major contribution to their **magnetic properties**.
- ✓ Depending up on the magnetic susceptibility( $\chi$ ) values, the materials are mainly classified into **diamagnetic** ( $\chi \ll 1$ ), **paramagnetic** ( $\chi > 1$ ), and **ferromagnetic** ( $\chi \gg 1$ ).
- ✓ Magnetic susceptibility( $\chi$ ) is temperature **independent** for diamagnetic materials whereas strongly **dependent** for para and ferromagnetic materials.
- ✓ The phenomenon of the alignment of magnetic dipoles in external magnetic field is termed as **Magnetization**. However, the magnetic dipoles restore their original state when field is switched off. This is called as **demagnetization**.
- ✓ If the demagnetization of paramagnetic substance occurs adiabatically, the atomic dipoles attain their original distribution in expense of their internal energy which results the drop in the temperature the substance. The process heating/cooling of a paramagnetic substance due to magnetization/demagnetization is known as **magneto-caloric effect**.
- ✓ The process of adiabatic demagnetization of paramagnetic substances may result **ultra low temperatures**.

# Magnetic work and adiabatic cooling

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## 12.7 Exercises

### Long answer type questions

- Q.1.** Differentiate between mechanical and non-mechanical forms of thermodynamic works with examples.
- Q.2.** Deduce general expression for the pressure-volume work.
- Q.3.** Discuss the phenomenon of dielectric polarization and hence derive the expression for the work.
- Q.4.** What is magnetization? Discuss how magnetization is affected by temperature for a paramagnetic material.
- Q.5.** Define magnetic susceptibility. Discuss its temperature dependence for ferromagnetic materials.
- Q.6.** What is adiabatic demagnetization? Explain how it could be utilized to achieve ultra low temperatures?
- Q.7.** Discuss the process of adiabatic cooling with the help of entropy-temperature behavior of paramagnetic specimen.

### Short answer type questions

- Q.1.** What is magnetic work?
- Q.2.** Discuss the origin of dia, para, and ferromagnetism.
- Q.3.** The magnetic susceptibility of diamagnetic materials is temperature independent. Why?
- Q.4.** What is magneto-caloric effect?
- Q.5.** In adiabatic cooling process, the paramagnetic specimen is first cooled to a lower temperature (liquid helium temperature). Why?

### Objective questions

- 1 Main contribution to the magnetic properties of materials are due to  
(a) orbital motion of the electrons

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- (b) spin motion of electrons
  - (c) both orbital and spin motions of the electrons
  - (d) nuclear magnetic moment
- 2 The magnetic susceptibility of diamagnetic materials is
- (a) directly proportional to the temperature
  - (b) independent of the temperature
  - (c) always positive
  - (d) less than 1
- 3 The magnetic susceptibility of paramagnetic materials is
- (a) directly proportional to the temperature
  - (b) inversely proportional to the temperature
  - (c) always negative
  - (d) less than 0
- 4 During magnetization, the entropy of the material
- (a) remains constant
  - (b) decreases
  - (c) increases
  - (d) none of the above
- 5 The Curie's law is given by
- (a)  $\chi \propto T$
  - (b)  $\chi \propto T^2$
  - (c)  $\chi \propto T^{-1}$
  - (d)  $\chi \propto T^{-2}$
- 6 In the presence of external magnetic field, the magnetic entropy of paramagnetic sample;
- (a) increases
  - (b) decreases
  - (c) remains constant
  - (d) is always zero

### 12.8 Glossary

**Induced magnetic dipoles:** In diamagnetic substances, the magnetic moment of the constituent atoms/molecules is zero. However, on the application of sufficient external magnetic field, the electron's motion gets modified to exhibit a non-zero magnetic moment on the constituent atoms/molecules. It is called as induced magnetic dipole moment.

**Residual magnetization:** The ferromagnetic materials possess larger values of magnetic susceptibility and exhibit greater magnetization when placed in external magnetic field and when field is switched off, net magnetization do not become zero. The material retains



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significant degree of magnetization due to the exchange interaction between the constituent atoms. This is termed as residual magnetization.

**Dewar vessel:** These are special types of vacuum flask used for storing low temperature liquids such as liquid nitrogen or liquid helium whose boiling points are much lower than room temperature. All dewars have walls constructed from two or more layers, with a high vacuum maintained between the layers.

**Curie's Law:** The magnetization of the paramagnetic material is (approximately) directly proportional to an applied magnetic field. Moreover, the magnetization is inversely proportional to temperature of the paramagnetic material (at constant field). This fact was introduced by Curie (law) and may be expressed as;

$$\chi \left( = \frac{M}{H} \right) \propto \frac{1}{T}$$

**Solenoid:** It refers specifically to a long, thin loop of wire, wrapped around a metallic core, which produces a uniform magnetic field in a volume of space on passing an electric current through it.

**Toroid:** A toroid is a coil of insulated wire wound on a donut-shaped form made of powdered iron. It is used as an inductor in electronic circuits.

### 12.9 References

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- 2 Thermal Physics by Garg, Bansal and Ghosh (Tata McGra-Hill, 1993).

**Further readings**

1. Thermodynamics by Enrico Fermi (Courier Dover Publications, 1956)
2. A Treatise on Heat: Including Kinetic Theory of Gases, Thermodynamics and Recent advances in Statistical Thermodynamics by Meghnad Saha, B.N. Srivastava (Indian Press, 1958).