

**MODULE 4**

Unit 1	Phase Transitions
Unit 2	Throttling Process and Free Expansion of a Gas
Unit 3	Production of Low Temperature
Unit 4	Phenomena at Low Temperature and the Third Law of Thermodynamics

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**1.0 INTRODUCTION**

In module 1 unit 1, we discussed change of state and it was mentioned that change of phase or phase transition is a special case of change of state. Phase transition is the transformation of a thermodynamic system from one phase of matter to another. This unit is devoted to phase transition. An important thing to note during phase change is that addition or withdrawal of heat to or from a substance does not result in change of temperature. When matter changes from one phase to another, energy is involved.

**2.0 A: OBJECTIVES**

By the end of this unit, you should be able to:

- define phase transition;

- give conditions under which phase transition occurs;
- differentiate between phase transition and change of state;
- derive Clapeyron's equation; and
- explain the three types of phase transitions.

## 2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

## 3.0 MAIN CONTENT

### 3.1 Phases of Matter

Matter or substance can exist in three (3) familiar phases namely; solid phase, liquid phase, gaseous phase. Matter of some substances can also exist in two (2) less familiar phases namely; super fluid phase, and plasma phase.

**Solid Phase:** Molecules are arranged in a closely packed form called crystal. These molecules can only vibrate about their lattice point.

**Liquid Phase:** Molecules are close together and they take the shape of the container. Molecules of liquid, within its volume, can move from place to place, rotate and vibrate.

**Gaseous Phase:** Molecules are widely separated and free to move around freely.

**Super fluid:** A supercritical (or critical) fluid is a liquid/gas under extreme pressure.

**Plasma:** Plasma is a gas that is composed of free-floating ions and free electrons.

#### 3.1.1 Phase Diagram

Figure 14.1 shows the phase diagram for water. The three regions for the three phases are shown in the diagram. The solid curves or lines represent boundary between two phases e.g. fusion curve is the boundary between solid phase and liquid phase. These lines are called equilibrium lines. The implication of this is that under specific

conditions of temperature and pressure, a substance can exist in equilibrium in more than one phase at the same time.

**Triple Point:** This is the point where the three equilibrium lines meet as indicated in the phase diagram 14.1 below. At the triple point, solid, liquid, and vapour phases of a pure substance coexist in equilibrium. The triple point values for common materials are given in table 14.1.

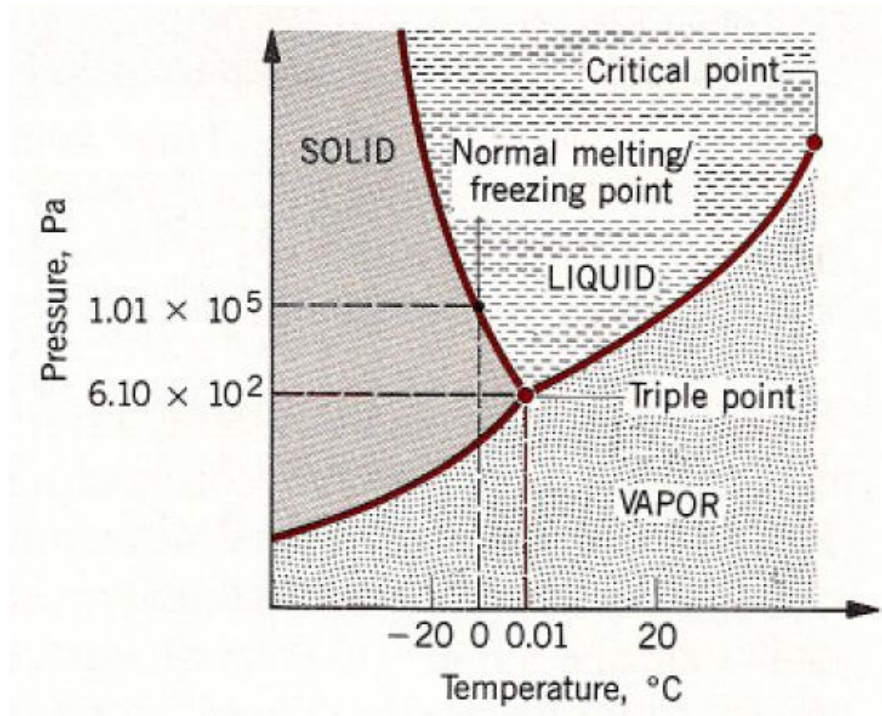
**NOTE:** All substances have triple point except Helium.

**Triple Point Temperature:** this is the temperature at which solid, liquid, and vapour phases coexist in equilibrium.

**Triple Point Pressure:** This is the pressure at which solid, liquid, and vapour phases coexist in equilibrium.

**Critical Point:** This specifies the conditions of temperature and pressure beyond which it is no longer possible to distinguish a liquid from a gas. The point is indicated in the phase diagram in figure 14.1 and the region beyond the critical point is known as fluid region.

The values of triple point and critical point temperature and pressure for some materials are given in table 14.1



**Fig. 14.1:** Phase Diagram for Water (After Cutnell and Johnson)

**Table 14.1 : Triple Point and Critical Point Conditions for some Common Materials**

Substance	Triple Point		Critical Point	
	Temperature (°C)	Pressure (Pa)	Temperature (°C)	Pressure (Pa)
Ammonia	-77.8	$6.05 \times 10^3$	132.4	$11.30 \times 10^6$
Carbon dioxide	-56.6	$5.18 \times 10^5$	31.1	$7.38 \times 10^6$
Hydrogen	-259.3	$7.04 \times 10^3$	-239.9	$1.30 \times 10^6$
Nitrogen	-210.0	$1.25 \times 10^4$	-146.9	$3.40 \times 10^6$
Oxygen	-218.8	$1.52 \times 10^2$	118.4	$5.08 \times 10^6$
Sulfur dioxide	75.5	$1.67 \times 10^3$	157.6	$7.88 \times 10^6$
Water	0.01	$6.10 \times 10^2$	374.3	$22.10 \times 10^6$

Source: Physics by John D. Cutnell and Kenneth W. Johnson

### 3.1.2 Co-exist Phases

This is when more than one phase of a substance (e.g. liquid-solid) exists side-by-side in equilibrium at the same time. For example, solid water and liquid water can coexist at 0 °C along the process of fusion or melting. The Gibbs energy ( $G$ ) for two coexisting phases  $\alpha$  and  $\beta$  of a pure substance are equal.

$$G^\alpha = G^\beta \quad 14.1$$

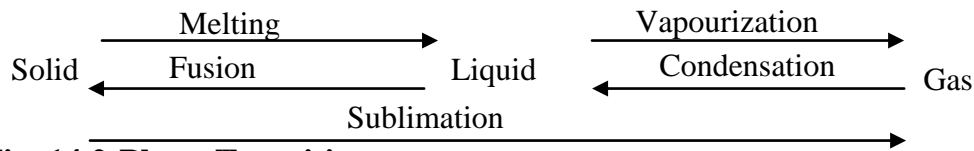
Using the phase diagram 14.1 for water as example, coexistence of phases occurs only along the equilibrium lines.

### 3.2 Phase Transitions

Phase transition occurs when matter changes from one of the phases of matter to another. The process always involves withdrawal or addition of heat energy from or to the matter. Using figure 14.1 as an illustration, phase transition occurs whenever any one of the curves in the phase diagram is crossed.

Phase transition for a pure substance occurs at constant temperature and pressure. The implication of this statement is that, for a pure substance  $dT = dP = 0$  during a phase change. However, the extensive thermodynamic coordinates or properties (e.g. Volume) change abruptly as a result of a phase transition. Internal energy ( $U$ ), enthalpy ( $H$ ), and entropy ( $S$ ) may also change during a phase transition.

Figure 14.2 shown the three most common phases of matter and the name given to each of the phase transitions.



**Fig. 14.2:Phase Transitions**

### 3.2.1 Latent Heat, $L$ , during Phase Transition

Latent heat  $L$  is the amount of heat energy per mole that must be added or removed when a substance changes from one phase to another. If the phase transition takes place reversibly, the heat transfer (i.e. latent heat) per mole for transition from initial phase  $\alpha$  to a final phase  $\beta$  is given by

$$L = T(S^\beta - S^\alpha) \quad 14.2$$

### 3.3 Types of Phase Transition

The three types of phase transitions are: first order, second order and lambda phase transitions.

#### 3.3.1 First Order Phase Transition

The phase transitions that we are familiar with i.e. sublimation, vaporization and fusion are called first order phase transition. They are called first order because the first order derivatives of the Gibbs function are finite.

Therefore, for a first order phase transition:

- there are changes in entropy and volume, and
- the first-order derivatives of the Gibbs function change discontinuously.

The characteristics of the first order phase transition are shown in figure 14.3. The specific heat capacity at constant pressure is infinite, this is because temperature is constant during phase change ( $C_p = T \left. \frac{\partial S}{\partial T} \right|_P$ ).

#### 3.3.2 Second Order Phase Transition

This is a phase transition in which the second derivatives of Gibbs are finite.

For order phase transition,

- T, P, G, S, and V (also H, U, and F) remain unchanged
- $C_P$ ,  $\beta$ , and  $\kappa$  (i.e from second derivatives of G) are finite

The only example of second order phase transition is the transition for the superconductor from superconducting to the normal state in zero magnetic field.

### 3.3.3 Lambda phase transition

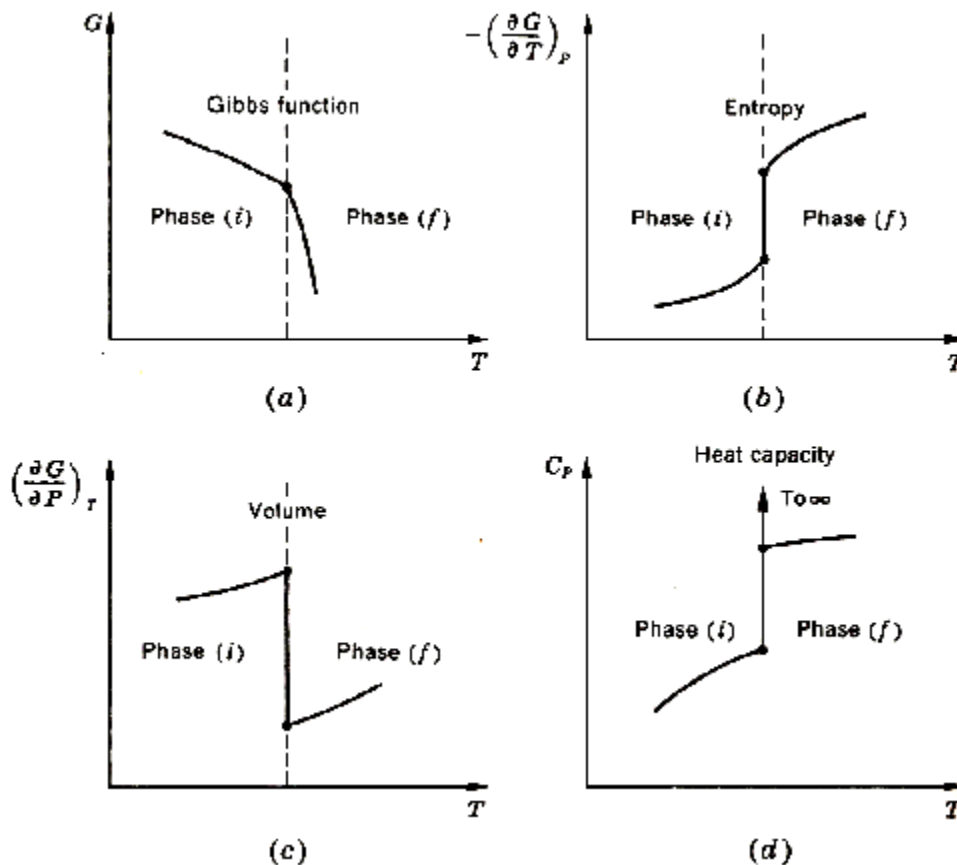
For the lambda phase transition:

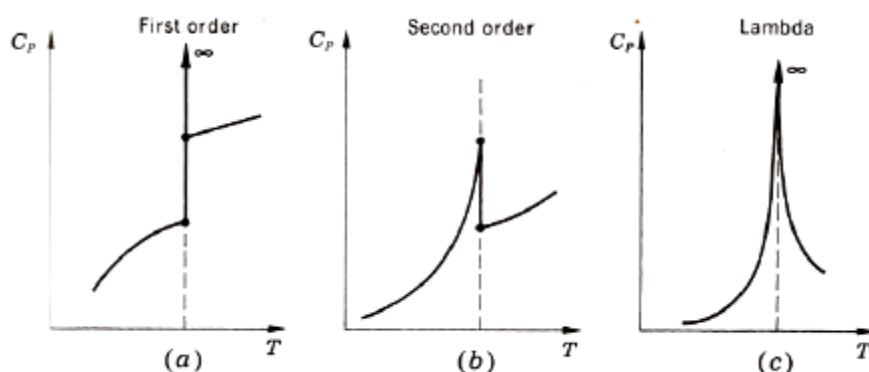
- T, P, and G remain constant,
- S and V (also U, H, and F) remain constant, and
- $C_P$ ,  $\beta$ , and  $\kappa$  are infinite

The most interesting example of lambda transition is the transition from ordinary liquid helium to super fluid helium at a temperature and corresponding pressure known as a lambda point.

Figure 14.4 shows the variation of  $C_P$  with temperature for each of the three phase transitions.

**Fig. 14.3: Characteristics of First Order Phase Transition (After Zemansky and Dittman)**





**Fig. 14.4:** The Three Types of Phase Transitions (After Zemansky and Dittman)

### 3.4 Gibbs Function during Phase Transition

The Gibbs function  $G$  does not change during phase transition.  
For coexisting phases,

$$dG|_{T,P} = 0 \quad 14.3$$

i.e. change in Gibbs at constant temperature and pressure is zero.

As mention earlier, two phases (e.g. liquid-gas) can coexist in equilibrium. For coexisting phases  $\alpha$  and  $\beta$  of a pure substance

$$G^\alpha = G^\beta \quad \Rightarrow \quad dG^\alpha = dG^\beta \quad 14.4$$

The Gibbs function  $G$  is given by equation 14.5 below. For your reference check block 1

$$dG = -SdT + VdP \quad 14.5$$

#### **Block 1**

$$G = U - ST + PV$$

Differentiating  $G$  gives

$$dG = dU - SdT - TdS + PdV + VdP$$

but  $dU = TdS - PdV$ , then

$$dG = -SdT + VdP$$

If equation 14.5 is put in equation 14.4, we obtain

$$-S^{\alpha}dT + V^{\alpha}dP = -S^{\beta}dT + V^{\beta}dP \quad 14.6$$

Rearranging (14.6) to obtain

$$\frac{dP}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} \quad 14.7$$

From equation 14.2

$$S^{\beta} - S^{\alpha} = \frac{L}{T} \quad 14.8$$

Then, put equation 14.8 in equation 14.7 to obtain

$$\frac{dp}{dT} = \frac{L}{T(V^{\beta} - V^{\alpha})} \quad 14.9$$

Equation 14.9 is known as the Clapeyron's equation.

If solid phase is labeled 1, liquid 2, and gas or vapour phase 3, equation 14.9 can be written as follows:

For solid – vapour phase transition, we have

$$\left(\frac{dP}{dT}\right)_{13} = \frac{L_{13}}{T(V^3 - V^1)}, \quad 14.10$$

where  $L_{13}$  is the latent heat of sublimation.

And for solid - liquid phase transition, we have

$$\left(\frac{dP}{dT}\right)_{12} = \frac{L_{12}}{T(V^2 - V^1)}, \quad 14.11$$

where  $L_{12}$  is the latent heat of fusion,



**SELF ASSESSMENT EXERCISE 1**

- i. Explain the following:  
(a) Phase transition (b) Triple point (c) Triple point temperature (d) Critical point.
- ii. Derive Clapeyron's equation.
- iii. The vapour pressure of a particular solid and a liquid of the same material are given by  $\ln P = 0.04 - \frac{6}{T}$  and  $\ln P = 0.03 - \frac{4}{T}$  respectively, where P is given in atmospheres. Find the temperature and pressure of the triple point of this material.

**3.5 Usefulness of Clapeyron's Equation**

Equation 14.9 can be integrated to obtain an expression for pressure as a function of temperature. If the following assumptions holds i.e. if the variation in latent heat can be negligible, and if one of the phases is a vapour, and if the vapour is assumed to be an ideal gas, and if the specific volume of the liquid or solid is neglected in comparison with that of the vapour, the integration can be readily carried out.

$$\left(\frac{dP}{dT}\right)_{23} = \frac{L_{23}}{T(RT/P)} \quad 14.12$$

$$\int \frac{dP}{P} = \frac{L_{23}}{R} \int \frac{dT}{T^2} \quad 14.13$$

Then,

$$\ln P = -\frac{L_{23}}{RT} + \ln \text{constant} \quad 14.14$$

**4.0 CONCLUSION**

Matter can exist in three well-known phases i.e. solid, liquid and gaseous phases. Phase transition occurs when changes from one phase to another. During the phase change, the heat added does not bring about a change in temperature. This type of heat is called latent heat of transformation (**L**). Gibbs free energy is a useful thermodynamic potential in describing phase transition.

**5.0 SUMMARY**

In this unit you have learnt that:

- matter can exist in three main phases namely; solid, liquid and gas phases
- two phases of matter can coexist in equilibrium
- phase transition occurs when matter changes from one of the phases of matter to another

- phase transition for a pure substance occurs at constant temperature and pressure
- there are three types of phase transition namely; first order, second order and lambda phase transitions
- the heat transfer (i.e. latent heat) per mole for transition from initial phase  $\alpha$  to a final phase  $\beta$  is  $L = T(S^\beta - S^\alpha)$
- the Clapeyron's equation for the first order transition is  $\frac{dp}{dT} = \frac{L}{T(V^\beta - V^\alpha)}$ .

## 6.0 TUTOR-MARKED ASSIGNMENT

- Name and describe the three types of phase transition.
- Differentiate between a change of state and phase transition.
- Define phase transition
- Give condition under which phase transition occurs

## 7.0 REFERENCES/FURTHER READING

- Adams, S. & Allday, J. (2000). *Advanced Physics*. Oxford University Press, UK.
- Bueche, F. J. & Hecht, E. (2006). *College physics*. Schaum's Outline Series. New York: McGraw-Hill.
- Cutnell, J. D. & Johnson, K. W. (1989). *Physics*. USA: John Wiley & Sons, Inc.
- Gibbs, K (2011). *Advanced physics, 2<sup>nd</sup> ed*. Cambridge: Cambridge University Press.
- Halliday, D., Resnick, R. & Walker, J. (2001). *Fundamentals of Physics-Extended (Sixth edition)*. New York: John Wiley and Sons, Inc..
- Palmer, B. S. & Rogalski, M. S. (1996). *Advance University Physics*, Gordon and Breach Science Publisher SA.
- Rao, Y. V. C. (2004). *An Introduction to Thermodynamics (Revised Edition)*. India: University Press (India) Private Limited.
- Sears, W. F. & Salinger, G. L. (1975). *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics (Third Edition)*. Philippines Addison-Wesley Publishing Company, Inc..
- Stroud, K. A. (1996). *Further Engineering Mathematics (Third Edition)*. London: Macmillan Press Limited.
- Vuille, C., Serway, R. A. & Faughn, J. S. (2009). *College physics, 8<sup>th</sup> ed*. Belmont, USA: Brooks/Cole.
- Zemansky, M. W. & Dittmann, R. H. (1981). *Heat and Thermodynamics (Sixth Edition)*. New York: McGraw-Hill Book Company.

## UNIT 2 THROTTLING PROCESS AND FREE EXPANSION OF A GAS

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- 2.0 A. Objectives
  - B. How to Study this Unit
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- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment
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### 1.0 INTRODUCTION

You were told in module 3, unit 2 that thermodynamic potentials are used to describe physical processes. In this unit, we are going to use the enthalpy  $\mathbf{H}$  to describe throttling process and the internal energy  $\mathbf{U}$  to describes free expansion of a gas

### 2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- explain throttling process;
- show that the initial and final enthalpies during a throttling process are equal;
- explain free expansion of a gas; and
- show that for free expansion of ideal gas at constant temperature,  $(\frac{\partial U}{\partial P})_T = 0$ .

### 2.0 B: HOW TO STUDY THIS UNIT

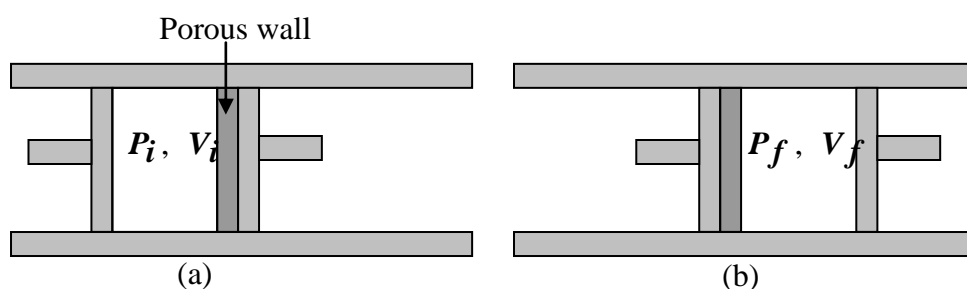
1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.

4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

### 3.0 MAIN CONTENT

#### 3.1 Throttling Process

Throttling Process is an irreversible steady flow expansion process in which a perfect gas is expanded through an orifice of minute dimensions such as a narrow throat of a slightly opened valve. During the process, the fluid passes through a narrow opening (a needle valve) from a region of constant high pressure to a region of constantly lower pressure adiabatically. Throttling is also known as Joule-Kelvin expansion.



**Fig. 15.1: A Throttling Process**

Consider a cylinder that is thermally insulated and equipped with two non-conducting pistons on the opposite sides of a porous wall as shown in figure 15.1. As indicated in figure 15.1 (a), the left hand side of the porous plug is filled with gas at  $P_i$  and  $V_i$  while the right hand side is empty. Suppose the two pistons are moved simultaneously to the right in such a way that a constant pressure  $P_i$  is maintained on the right hand side of the wall while a constant lower pressure  $P_f$  is maintained on the right hand side. After all the gas has seeped through the porous wall, the final equilibrium state of the system is shown in figure 15.1 (b). This kind of process is known as throttling process.

A throttling process is an irreversible process. This is because the gas passes through non-equilibrium states on its way from initial equilibrium state to its final equilibrium state. As you know, non-equilibrium states cannot be described by thermodynamic coordinates i.e. the non-equilibrium states between the initial and final equilibrium states during a throttling process cannot be described using thermodynamic coordinates. But we can make an interesting conclusion from the initial and final equilibrium states.

##### 3.1.1 Enthalpy during throttling process

One of the most interesting properties of the enthalpy function ( $H$ ) is in connection with a throttling process.

The equation of the first law of thermodynamics is

$$dQ = dU - W \quad 15.1$$

but throttling process occurs adiabatically,

$$dQ = 0 \quad (\text{adiabatic process}) \quad 15.2$$

Then, the first law of thermodynamics becomes

$$dU = W \quad 15.3$$

and work

$$W = - \int_0^{V_f} P_f dV - \int_{V_i}^0 P_i dV \quad 15.4$$

Since both pressures ( $P_i$  and  $P_f$ ) remain constant, equation 15.3 becomes

$$W = -(P_f V_f - P_i V_i) \quad 15.5$$

Now, put equation 15.5 in 15.3 to obtain

$$U_f - U_i = P_f V_f - P_i V_i$$

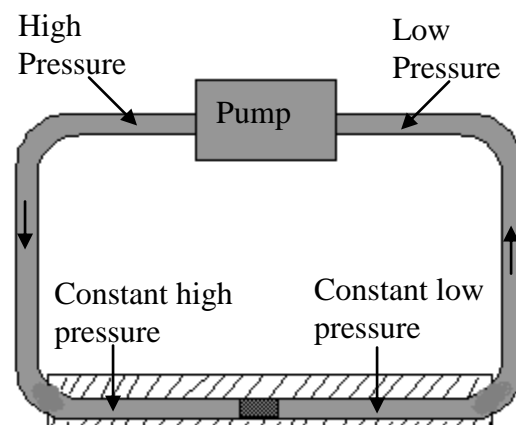
Rearranging gives

$$U_i - P_i V_i = U_f - P_f V_f \quad 15.6$$

But enthalpy  $H = U - PV$ , so 15.6 becomes

$$H_i = H_f \quad 15.7$$

In a throttling process, therefore, the initial and final enthalpies are equal.



**Figure 15.2:** Apparatus for Performing a Continuous Throttling Process

Throttling process is very useful in refrigeration. A continuous throttling process can be achieved using the apparatus shown in figure 15.2.

### SELF ASSESSMENT EXERCISE 1

- i. What is a throttling process
- ii. For a throttling process, show that initial enthalpy  $H_i$  is equal to final enthalpy  $H_f$ .

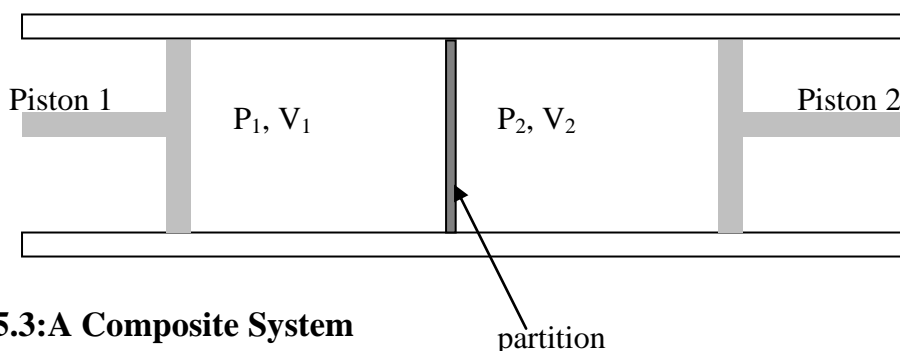
### 3.2 Free Expansion of a Gas

The concept of work done by or on a system has been treated in module 2, unit 1 under the first law of thermodynamics. The work done by or on a gas in a cylinder with a moveable piston was derived to be

$$dW = -PdV \quad 15.8$$

Equation 15.8 above is as a result of expansion or compression of a gas in a cylinder. That is, in the case of expansion, the molecules move faster and push the piston (exerted a force on the piston) and move the piston through a distance.

Now consider, for example, a composite system consisting of a hydrostatic fluid in the compartments 1 and 2 with  $(P_1, V_1)$  and  $(P_2, V_2)$  respectively as shown in figure 15.3 below.



**Fig. 15.3:**A Composite System

Each compartment or both compartments can undergo an adiabatic work by interacting with the surroundings. This may be done by moving one or both of the pistons in or out, either slowly (a quasi-static process) so that the work done  $W = -\int PdV$ , with pressure  $P$  being equal to the equilibrium value (i.e. for a quasi-static process the system is in equilibrium at every instant). Also the piston can be moved very rapidly (a non-quasi-static process) so that the pressure at the face is less than the equilibrium value. For these two examples, work is done on the piston due to expansion of the fluid.

However, if either or both of the pistons is or are pulled out at a faster rate than the velocity of the molecules of the fluid, the fluid will do no work on the piston at all. This type of process is called a free expansion of a gas. Another good example of this process is described below.

Suppose the system in figure 15.3 is thermally insulated and that compartment 1 contains a gas while the other compartment is empty. If the partition is removed, the gas will undergo what is known as a free expansion in which no work is done and no heat is transferred. From the first law of thermodynamics, since both  $Q$  and  $W$  are zero, it follows that the internal energy remains unchanged during a free expansion.

For free expansion of gas, work is zero ( $W = 0$ ) and no heat is transfer ( $Q = 0$ ). The equation of the first law of thermodynamic reduces to

$$dU = 0 \quad 15.9$$

### 3.2.1 Temperature Change during Free Expansion

The value of temperature change  $(\frac{\partial T}{\partial V})_U$  during free expansion process has engaged the attention of physicists for over 100 years. Joule in 1843, and many others attempted to measure either the quantity  $(\frac{\partial T}{\partial V})_U$ , which may be called the Joule Coefficient, or related quantities that are all a measure of the effect of a free expansion-often called the Joule effect. The results of their experiments showed that  $(\frac{\partial T}{\partial V})_U = 0$  for ideal gas, but not for real gas (already discussed in module 2, unit 2).

### 3.2.2 Internal Energy U during Free Expansion

The internal energy  $U$  of a gas, like any state function, is a function of any two of the coordinates  $P$ ,  $V$ , and  $T$ .

Now consider  $U$  as a function of  $T$  and  $V$  i.e.  $U(T, V)$ , then the derivative of  $U$  is

$$dU = (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV \quad 15.10$$

If the temperature change is equal to zero (i.e.  $dT = 0$ ), and for free expansion ( $dU = 0$ ), then equation 15.10 becomes

$$(\frac{\partial U}{\partial V})_T = 0 \quad 15.11$$

Equation (15.11) implies that  $U$  does not depend on  $V$ .

Also consider  $U$  as a function of  $T$  and  $P$  i.e.  $U(T, P)$ , the derivative of  $U$  is

$$dU = (\frac{\partial U}{\partial T})_P dT + (\frac{\partial U}{\partial P})_T dP \quad 15.12$$

If the temperature change is equal to zero (i.e.  $dT = 0$ ) and for free expansion ( $dU = 0$ ), then equation 15.12 becomes

$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \quad 15.13$$

Equation 15.13 implies that  $U$  does not depend on  $P$ .

These (i.e. equation 15.11 and 15.13) follows that if no temperature change takes place in a free expansion process,  $U$  is independent of  $V$  and  $P$ , and therefore  $U$  is a function of  $T$  only. This result, of course, has been obtained in Module 2, unit 2, under Gay-Lussac-Joule experiment.

## SELF ASSESSMENT EXERCISE 2

- i. Explain Throttling Process.
- ii. One mole of an ideal gas undergoes a throttling process from pressure of  $4.052 \times 10^5 \text{ Nm}^{-2}$  to  $1.013 \times 10^5 \text{ Nm}^{-2}$ . The initial temperature of the gas is  $50^\circ\text{C}$ . (a) How much work could have been done by the ideal gas has it undergone a reversible process to the same final state at constant temperature? (b) How much does the entropy of the universe increase as a result of the throttling process? ( $R=8.3 \text{ JK}^{-1}\text{mol}^{-1}$ )

## 4.0 CONCLUSION

Throttling process can be described using the enthalpy  $H$  of the system. During a throttling process, the enthalpy  $H$  is constant. This process is useful in refrigeration. Free expansion of a gas can be described using the internal energy of the system.

## 5.0 SUMMARY

In this unit you have learnt that:

- during the process, the fluid passes through a narrow opening (a needle valve) from a region of constant high pressure to a region of constantly lower pressure adiabatically
- the enthalpy  $H$  can be used to describe a throttling process
- for a throttling process, the initial enthalpy is equal to the final enthalpy (i.e.  $H_i = H_f$ )
- throttling process is very useful in refrigeration
- free expansion of a gas that occurs adiabatically, work is zero ( $W = 0$ ) and no heat is transfer ( $Q = 0$ ), hence from the first law  $dU = 0$
- for free expansion process for an ideal gas, the internal energy  $U$  is a function of temperature alone i.e.  $\left(\frac{\partial U}{\partial P}\right)_T = 0$ .



## 6.0 TUTOR-MARKED ASSIGNMENT

1. Explain what is meant by free expansion of a gas.
2. 1 mol of an ideal gas for which  $C_V = 25.12$  and  $C_P = 33.44$  J/mol K expands adiabatically from an initial state at 340 K and 500 Pa to a final state where its volume has doubled. Find the final temperature of the gas, the work done, and the entropy change of the gas, for (a) a reversible expansion and (b) a free expansion of the gas into an evacuated space (Joule expansion). (1 Pa =  $1.013 \times 10^5$  Nm<sup>-2</sup>).
3. Show that the initial and final enthalpies during a throttling process are equal.
4. Show that for free expansion of ideal gas at constant temperature

$$\left(\frac{\partial \mu}{\partial \rho}\right)_T = 0$$

## 7.0 REFERENCES/FURTHER READING

- Adams, S. & Allday, J. (2000). *Advanced Physics*. Oxford University Press, UK.
- Bueche, F. J. & Hecht, E. (2006). *College physics*. Schaum's Outline Series. New York: McGraw-Hill.
- Cutnell, J. D. & Johnson, K. W. (1989). *Physics*. USA: John Wiley & Sons, Inc.
- Gibbs, K (2011). *Advanced physics, 2<sup>nd</sup> ed*. Cambridge: Cambridge University Press.
- Halliday, D., Resnick, R. & Walker, J. (2001). *Fundamentals of Physics-Extended (Sixth edition)*. New York: John Wiley and Sons, Inc..
- Palmer, B. S. & Rogalski, M. S. (1996). *Advance University Physics*, Gordon and Breach Science Publisher SA.
- Rao, Y. V. C. (2004). *An Introduction to Thermodynamics (Revised Edition)*. India: University Press (India) Private Limited.
- Sears, W. F. & Salinger, G. L. (1975). *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics (Third Edition)*. Philippines Addison-Wesley Publishing Company, Inc..
- Stroud, K. A. (1996). *Further Engineering Mathematics (Third Edition)*. London: Macmillan Press Limited.
- Vuille, C., Serway, R. A. & Faughn, J. S. (2009). *College physics, 8<sup>th</sup> ed*. Belmont, USA: Brooks/Cole.
- Zemansky, M. W. & Dittmann, R. H. (1981). *Heat and Thermodynamics (Sixth Edition)*. New York: McGraw-Hill Book Company.

## UNIT 3 PRODUCTION OF LOW TEMPERATURE

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### 1.0 INTRODUCTION

We discussed in module 2, unit 5, the device used in lowering the temperature of a body or system i.e. refrigerator. We will discuss in this unit, the cooling method that is being used to obtain extremely low temperature i.e. cooling by adiabatic demagnetisation.

### 2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- discuss the process of cooling;
- mention different methods being used to achieve low temperature;
- discuss the process of cooling by adiabatic demagnetization; and
- derive the expression for change in temperature with respect to field  $\mathbf{B}$  at constant entropy i.e.  $(\frac{\partial T}{\partial B})_S$ .

### 2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators

and by consulting other relevant materials or internet.

3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

### 3.0 MAIN CONTENT

#### 3.1 Cooling Process

Generally, two processes are involved in cooling a gas namely; isothermal process followed by adiabatic process. For example, to cool a gas by adiabatic decompression, the gas is first compressed isothermally i.e. at constant temperature. This is done by compressing the gas in a vessel that is not insulated and wait long enough for the gas to lose any heat that is generated due to compression. In this way, a constant temperature is maintained. The heat that is generated can be explained in terms of the law  $\frac{PV}{T} = \text{constant}$ . Then, the vessel containing the gas is insulated and the gas is allowed to expand adiabatically (i.e. no heat transfer is allowed between the vessel and the surrounding). This kind of expansion brings about reduction in temperature. The expression for change in temperature with respect to pressure at constant entropy  $(\frac{\partial T}{\partial P})_S$  can be derived. The process can be repeated until the desired temperature is reached. This method is called cooling by adiabatic decompression.

##### 3.1.1 Methods of Cooling

Some of the methods being used for low temperature cooling are:

- laser cooling
- evaporative cooling (e.g. evaporation of  $^3\text{He}$ )
- cooling by liquefaction
- cooling by adiabatic demagnetisation

The process of cooling by adiabatic demagnetisation has been used to obtain extremely low temperature. Cooling by adiabatic demagnetisation is therefore discussed below.

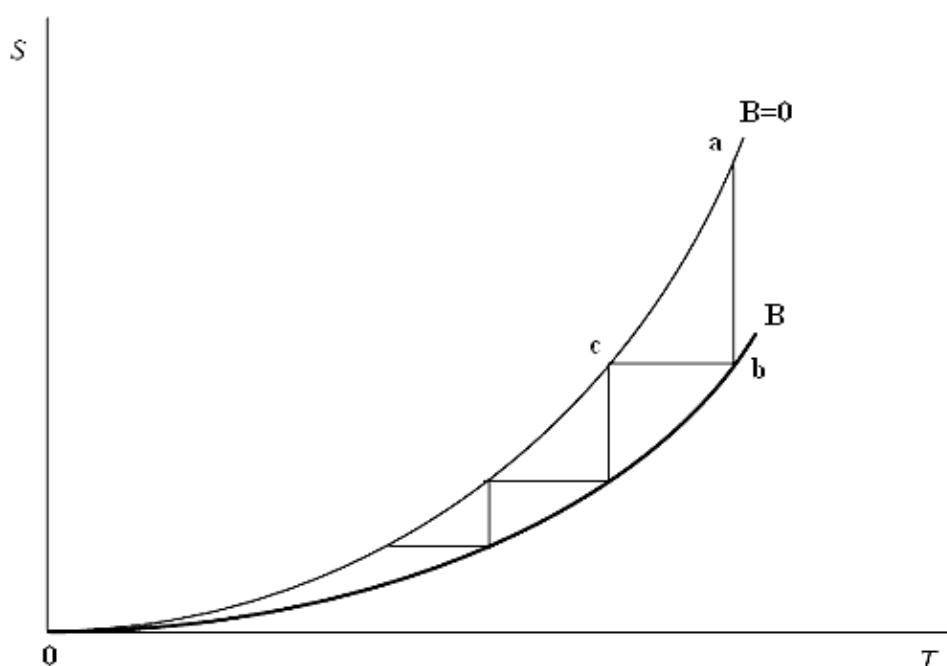
#### 3.2 Cooling by Adiabatic Demagnetisation

Different methods have been employed to obtain very low temperature. The method of adiabatic demagnetisation has been used to obtain extremely low temperature. Figure 16.1 shows the S-T diagram for adiabatic demagnetisation. Magnetic field  $B$  is zero along the curve labeled  $B = 0$  while magnetic field is  $B$  along the curve labeled  $B$ . In process **ab**, a sample of paramagnetic salt (e.g. cerium magnesium nitrate)

already cooled to low temperature by other means (e.g. by contact with a bath of liquid helium), is magnetized isothermally. The sample is often suspended in an atmosphere of helium, which can conduct away any heat that is produced, and hence keeps the process isothermal. Hence, process **ab** is isothermal magnetization. Then, in process **bc** (i.e. adiabatic demagnetisation), the paramagnetic salt is insulated (by pumping out the helium) and then demagnetized adiabatically. This process of isothermal magnetization followed by an adiabatic demagnetisation can be repeated over and over again until the desired temperature is reached. Temperature close to 0 K have been reached in this manner.

Note that one could actually reach a temperature of absolute zero if one did this an infinite number of time- but not for any fewer (statement of third law of thermodynamics).

**Fig. 16.1: The Temperature Dependence of the Entropy of a Magnetic System**



### 3.3 Theory of Adiabatic Demagnetisation

Magnetic dipole moment  $\mathbf{P}$  of a sample is the maximum torque it experiences in unit field  $\mathbf{B}$ . Torque is given by  $\tau = \mathbf{P} \times \mathbf{B}$ . The magnetization  $\mathbf{M}$  of a specimen is defined by  $\mathbf{B} = \mu\mathbf{H} = \mu_0(\mathbf{H} + \mathbf{M})$ . The magnetization is also equal to the magnetic moment per unit volume. The differential form of work for a magnetic system is  $BdM$  (Module 1, unit 5, section 3.1.1).

$$dW = BdM \quad 16.1$$

$BdM$  is the work done per unit volume on an isotropic sample in increasing its magnetization from  $M$  to  $M + dM$ .

If we add heat to a magnetisable sample, and do work per unit volume on it by putting it in a magnetic field  $B$  and thereby increase its magnetization by  $dM$ , then, provided there is no change in volume, the increase in its internal energy per unit volume is given by

$$dU = TdS + BdM \quad 16.2$$

In this magnetic context, we can define state functions  $H$ ,  $A$ , and  $G$  per unit volume by

$$H = U - BM \quad 16.3$$

$$A = U - TS \quad 16.4$$

$$G = H - TS = A - BM \quad 16.5$$

And the differential forms as,

$$dH = TdS - MdB \quad 16.6$$

$$dA = -SdT + BdM \quad 16.7$$

$$dG = -SdT - MdB \quad 16.8$$

$M$  is the dipole moment per unit volume, in  $\text{NmT}^{-1}\text{m}^{-3}$ , which is the same as the magnetization in  $\text{Am}^{-1}$

We can derive an expression for the lowering of the temperature in an adiabatic decompression  $(\frac{\partial T}{\partial P})_S$ . Also using the same argument, step-by-step, for the lowering of the temperature in an adiabatic demagnetisation  $(\frac{\partial T}{\partial B})_S$ .

### 3.3.1 Adiabatic Decompression $(\frac{\partial T}{\partial P})_S$

Considering entropy as a function of temperature and pressure (i. e.  $S(T,P)$ ),

$$(\frac{\partial S}{\partial T})_P (\frac{\partial T}{\partial P})_S (\frac{\partial P}{\partial S})_T = -1 \quad 16.9$$

In a reversible process  $dS = \frac{dQ}{T}$ , and in an isobaric process,

$$\begin{aligned} dQ &= C_P dT \\ \text{i.e. } TdS &= C_P dT \end{aligned} \quad 16.10$$

From equation 16.10, partial derivative of S with respect to T at constant pressure gives

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad 16.11$$

Also from a Maxwell relation,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad 16.12$$

From equation 16.9

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T \quad 16.13$$

Put equations 16.11 and 16.12 in 16.13 to obtain

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P \quad 16.14$$

If the gas is an ideal gas, the equation of state is  $PV = nRT$ , so that

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} = \frac{V}{T} \quad 16.15$$

Put equation 16.15 in 16.14

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{V}{C_P} \quad 16.15$$

### 3.3.2 Adiabatic Demagnetisation $\left(\frac{\partial T}{\partial B}\right)_S$

The same argument as above can be used for adiabatic demagnetisation  $\left(\frac{\partial T}{\partial B}\right)_S$ .

We can consider the entropy as a function of temperature and magnetic field i.e.  $S(T, B)$ , we have

$$\left(\frac{\partial S}{\partial T}\right)_B \left(\frac{\partial T}{\partial B}\right)_S \left(\frac{\partial B}{\partial S}\right)_T = -1 \quad 16.16$$

Then

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_B \left(\frac{\partial S}{\partial B}\right)_T \quad 16.17$$

In a reversible process  $dS = \frac{dQ}{T}$ , and in a constant magnetic field,  $dQ = C_B dT$ ,  $C_B$  is the heat capacity per unit volume (i.e. the heat required to raise the temperature of a unit volume by one degree)

In a constant magnetic field

$$\left(\frac{\partial S}{\partial T}\right)_B = \frac{C_B}{T} \quad 16.18$$

Also from a Maxwell relation corresponding to  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ , that is

$$\left(\frac{\partial S}{\partial B}\right)_T = -\left(\frac{\partial M}{\partial T}\right)_B \quad 16.19$$

Now for a paramagnetic material, the magnetization, for a given field is proportional to  $B$  and it falls off inversely as the temperature (that's the equation of state).

That is  $M = \frac{aB}{T}$

Therefore,

$$\left(\frac{\partial M}{\partial T}\right)_B = -\frac{aB}{T^2} = -\frac{M}{T} \quad 16.20$$

Put 16.20 in 16.19

$$\left(\frac{\partial S}{\partial B}\right)_T = \frac{M}{T} \quad 16.21$$

Now put equations 16.18 and 16.21 in 16.17, to obtain

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{M}{C_B} \quad 16.22$$

Equation 16.22 gives the cooling effect, i.e. the variation of temperature with magnetic field at constant entropy, in terms of magnetization  $M$  and heat capacity  $C_B$ .

The cooling effect is particularly effective at low temperature when  $C_B$  is small.

### 3.4 Entropy and Temperature

Cooling by adiabatic demagnetisation involves successive isothermal magnetizations followed by adiabatic demagnetisations, and this suggests that some insight into the process might be obtained by following it on an entropy-temperature (ST) diagram.

Using figure 16.1 above, the cooling effect  $(\frac{\partial T}{\partial B})_S$  is shown in the process **bc** as well as other subsequent processes indicated by the horizontal lines linking the two curves.

A complete cooling is indicated in processes **ab** and **bc**, which can be repeated until the desired temperature is achieved.

### SELF ASSESSMENT EXERCISE

- i. Give four methods of achieving low temperature and the minimum temperature attainable with each method.
- ii. Describe the process of cooling by adiabatic decompression.
- iii. Derive the expression for the change in temperature with respect to field **B** at constant entropy i.e.  $(\frac{\partial T}{\partial B})_S$

## 4.0 CONCLUSION

We have discussed in this unit a method of cooling being used to achieving extremely low temperature i.e. cooling by adiabatic demagnetisation. The refrigerator that does this is called adiabatic demagnetisation refrigerator. In the next unit, we are going to be looking at the phenomena at extremely low temperature, and then round up the course by stating the third law of thermodynamics i.e. the un-attainability of absolute zero.

## 5.0 SUMMARY

In this unit, you have learnt:

- about the process of cooling
- about methods being used for low temperature cooling
- about processes and relevant equations involve in cooling by adiabatic demagnetisation
- that the expression for change in temperature with respect to field **B** at constant entropy i.e.  $(\frac{\partial T}{\partial B})_S$ .

## 6.0 TUTOR-MARKED ASSIGNMENT

- i. Write the differential form of thermodynamic potential for a magnetic system.
- ii. Using an entropy-temperature (ST) diagram, describe the process of cooling by adiabatic demagnetisation.



## 7.0 REFERENCES/FURTHER READING

- Adams, S. & Allday, J. (2000). *Advanced Physics*. Oxford University Press, UK.
- Bueche, F. J. & Hecht, E. (2006). *College physics*. Schaum's Outline Series. New York: McGraw-Hill.
- Cutnell, J. D. & Johnson, K. W. (1989). *Physics*. USA: John Wiley & Sons, Inc.
- Gibbs, K (2011). *Advanced physics, 2<sup>nd</sup> ed*. Cambridge: Cambridge University Press.
- Halliday, D., Resnick, R. & Walker, J. (2001). *Fundamentals of Physics-Extended (Sixth edition)*. New York: John Wiley and Sons, Inc..
- Palmer, B. S. & Rogalski, M. S. (1996). *Advance University Physics*, Gordon and Breach Science Publisher SA.
- Rao, Y. V. C. (2004). *An Introduction to Thermodynamics (Revised Edition)*.India: University Press (India) Private Limited.
- Sears, W. F. & Salinger, G. L. (1975). *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*(Third Edition). Philippines Addison-Wesley Publishing Company, Inc..
- Stroud, K.A. (1996). *Further Engineering Mathematics (Third Edition)*. London: Macmillan Press Limited.
- Vuille, C., Serway, R. A. & Faughn, J. S. (2009). *College physics, 8<sup>th</sup> ed*. Belmont, USA: Brooks/Cole.
- Zemansky, M. W. & Dittmann, R. H. (1981). *Heat and Thermodynamics (Sixth Edition)*.New York: McGraw-Hill Book Company.

## UNIT 4 PHENOMENA AT LOW TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

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    - 3.1.1 Liquefaction of Gases
    - 3.1.2 Maintenance of Low Temperature
    - 3.1.3 Measurement of Low Temperature
  - 3.2 Phenomena at Low Temperature
    - 3.2.1 Superconductivity in Metals
    - 3.2.2 Superfluidity
  - 3.3 Application of Low Temperature Phenomena
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  - 3.4 Nernst Heat Theorem
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    - 3.5.1 The Statement of the Third Law of Thermodynamics
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- 5.0 Summary
- 6.0 Tutor-Marked Assignment
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### 1.0 INTRODUCTION

In the last unit, we discussed method of achieving low or extremely low temperature. The focus of this unit will be on the behaviours of materials at low temperature and then we round up our discussion by stating the third law of thermodynamics.

### 2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- explain the meaning of low temperature physics;
- explain some phenomenon at low temperature;
- mention useful applications of low temperature phenomenon;
- state Nernst heat theorem; and
- state third law of thermodynamics.

### 2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all

the answers.

2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

### **3.0 MAIN CONTENT**

#### **3.1 Low Temperature Physics**

Low temperature physics is a specialised area of physics that deals with the behaviour of materials at low or extremely low temperature. Now, the big question is this. How low is low? Low temperature, in this context, is the temperature low enough to observe the phenomena such as superconductivity and super-fluidity. Here, we are going to concentrate only on the meanings of these phenomena and their applications. The theory and the detail description of these two phenomena are beyond the scope of this unit.

##### **3.1.1 Liquefaction of Gases**

Liquefaction of gases is the process by which substances in their gaseous state are converted to the liquid state.

Liquefaction of gases can be achieved:

- by compressing the gas at temperatures less than its critical temperature;
- by making the gas do some kind of work against an external force, thereby causing the gas to lose energy and change to the liquid state; and
- by making the gas do work against its own internal forces, this also causing it to lose energy and liquefy.

When gases are liquefied, they can then be stored and transported in much more compact form than in the gaseous state. One kind of liquefied gas that we are familiar with is Liquefied Natural Gas (LNG). In principle, any gas can be liquefied, so their compactness and ease of transportation has made them popular for a number of other applications.

##### **Applications of Liquefaction**

Liquefied gases are used in the following application:

- Fuel for rocket engines e.g. liquefied oxygen and hydrogen;
- For welding operation e.g. liquid oxygen and acetylene;

- Aqualung devices e.g. combination of liquid oxygen and liquid nitrogen;
- For research application (cryogenics) e.g. liquid helium is widely used for the study of behaviour of matter at temperatures close to absolute zero.
- Liquid nitrogen for low temperature refrigeration.

### 3.1.2 Maintenance of Low Temperature

The method on maintaining low temperature is by using liquefied gases as heat sink. For example, some gases liquefy at quite low temperatures (e.g. nitrogen liquefied at 77 K, hydrogen at 20 K, helium at 4.2 K). If such gases are liquefied, the liquid can be used as bath to maintain experiment at these temperatures.

### 3.1.3 Measurement of Low Temperature

Conventional thermometers may be used at quite low temperatures. Table 17.1 gives the lowest temperature for some convectional thermometers.

**Table 17.1 : Lowest Temperature for some Conventional Thermometers**

Conventional Thermometer	Lowest Temperature
Platinum resistance thermometer	about 20 K
Indium resistance thermometer	about 4 K
Helium gas thermometer	about 3 K
Carbon resistors as thermometer	From 4 K to 0.1 K

## 3.2 Phenomena at Low Temperature

Two known phenomena at low temperature are superconductivity and superfluidity.

### 3.2.1 Superconductivity in Metals

At a temperature low enough, most metals as well as many alloys and compounds enters a state at which their resistant to flow of current disappears (i.e. they become a superconductor). This state is called superconductivity in metals. Most metals in the periodic table, many alloys and compounds show this behaviour. The implication of superconductivity is that if a superconductor is a wire loop and a current is generated in that loop, then it flows for years with no significant decay.

### 3.2.2 Superfluidity

At a temperature low enough, materials enter a state whereby they become fluid that flows with no viscosity. Superfluidity can only be observed at much lower temperatures than the temperature at which superconductivity is observed. For

example, helium-4 does not display superfluid-behaviour until it reaches a temperature below 2 K. Note that materials that become solid at low temperatures cannot become superfluids.

When a material becomes a superfluid, the following will be observed:

- Because superfluids have no internal viscosity, a vortex formed within a superfluid persists forever.
- A superfluid has zero thermodynamic entropy and infinite thermal conductivity, meaning that no temperature differential can exist between two superfluids or two parts of the same superfluid.
- A superfluid can also climb up and out of a container in a one-atom-thick layer if the container is not sealed.
- A conventional molecule embedded within a superfluid can move with full rotational freedom, behaving like a gas.

### 3.3 Application of Low Temperature Phenomena

Applications of low temperature phenomena are listed below:

#### 3.3.1 Applications of Superconductivity

Superconductivity promises a whole lot of applications but the limitation to this is how to maintain this temperature because the whole of these applications are at room temperature in everyday world.

Most significant real application of low temperature physics is the super-conducting magnet. This is being used for magnetic resonance imaging (MRI) and particle accelerators. Other applications are in;

- Supersensor,
- Quantum computing,
- Loss less power transmission line. We know that energy loss on a transmission line is  $I^2R$ . Imagining using super conduction as transmission cable, meaning that  $R = 0$  i.e.  $I^2R = 0$ .

#### 3.3.2 Applications of Superfluidity

Superfluidity does not have a wide range of application as superconductivity. The two areas of applications are in dilution refrigerators and spectroscopy.

### 3.4 Nernst Heat Theorem

Third law of thermodynamics explains the behaviour of systems, which are in internal equilibrium, as the temperature approaches absolute zero (i.e. 0 K).

Consider a chemical reaction taking place in a container at constant pressure, and that the container makes a contact with a heat reservoir at a temperature  $T$ . If the temperature of the system increases as a result of the reaction (i.e. if the reaction is exothermic) there will be a heat flow to the reservoir until the temperature of the system reduced to its original value  $T$ . Don't forget that a heat bath or reservoir is so large that its temperature does not change appreciably when heat flow in or out of it.

For a process at constant pressure the heat gain or lost is an increase or decrease in enthalpy. Then

$$\Delta H = H_f - H_i = -Q \quad 17.1$$

Minus sign in the right hand side of equation 17.1 indicates that heat flows out of the system. The heat of reaction is usually given as  $\Delta H$ .  $\Delta H$  is positive for an endothermic reaction and negative for exothermic reaction.

Change in the Gibbs function and change in enthalpy are related as

$$G_f - G_i = H_f - H_i + T \left( \frac{\partial(G_f - G_i)}{\partial T} \right)_P \quad 17.2$$

written as

$$\Delta G = \Delta H + T \left( \frac{\partial(\Delta G)}{\partial T} \right)_P \quad 17.3$$

This implies that change in enthalpy and change in Gibbs function are equal only when  $T \left( \frac{\partial \Delta G}{\partial T} \right)_P$  approaches zero. Nernst proposed that, in the limit, as the temperature approaches zero, the changes in enthalpy and Gibbs function are equal. Since

$$\left( \frac{\partial \Delta G}{\partial T} \right)_P = -\Delta S \quad 17.4$$

So that

$$\lim_{T \rightarrow 0} (\Delta S_1 - \Delta S_2) = 0 \quad 17.5$$

This implies that chemical reactions at a temperature of absolute zero take place with no change in entropy.

Planck later extended this to suppose that, not only does  $\Delta G \rightarrow \Delta H$ , but that, as  $T \rightarrow 0$ , the enthalpy and the Gibbs function of the system approach each other asymptotically in such a manner that, in the limit, as  $T \rightarrow 0$ ,  $G \rightarrow H$  and  $(\frac{\partial G}{\partial T})_P \rightarrow 0$ .

i.e.

$$\lim_{T \rightarrow 0} S = 0 \quad 17.6$$

### 3.5 Third Law of Thermodynamics

Nernst's heat theorem and Planck's extension of it, though derived from observing the behaviour of chemical reactions in solids and liquids, is now believed to apply quite generally to any process. Equation 17.6 is known as the third law of thermodynamics.

#### 3.5.1 The Statement of the Third Law of Thermodynamics

The third of thermodynamics states that it is impossible to reduce the temperature of a material body to the absolute zero of temperature in a finite number of operations.

This is the third law of thermodynamics, and it is an inevitable consequence of Planck's extension of Nernst's heat theorem. The third law is sometimes called the unattainability statement of the third law.

#### SELF ASSESSMENT EXERCISE 1

- i. What is low temperature physics?
- ii. Name the two phenomena at low temperature and explain each of them.
- iii. Derive equation 17.3 from the definitions of Enthalpy and Gibb's free energy.
- iv. State Nernst's heat theorem.

### 4.0 CONCLUSION

The quest by scientists to cool a body or a system to extremely low temperature (about 0 K) brought about discoveries, along the way, of two important phenomena of materials at extremely low temperature (i.e. superconductivity and superfluidity). These phenomena have a wide range of applications but the limitation is that these applications are relevant to our every day activity at room temperature. The process of cooling a body by gradual withdrawal of heat becomes more and more difficult as the absolute temperature is approach. This is the statement of the third law of thermodynamic i.e. it is impossible to reduce the temperature of a material body to the absolute zero of temperature in a finite number of operations.

## 5.0 SUMMARY

In this unit, you have learnt that:

- the properties of materials change dramatically at low temperature
- the phenomena at low temperature are superconductivity and superfluidity
- these phenomena have a wide range of applications but there is limitation i.e. the usage temperature of these applications
- the statement of the third law of thermodynamics is that bodies or systems can be cooled to absolute temperature by infinite number of operations.

## 6.0 TUTOR-MARKED ASSIGNMENT

- i. Explain the limitation of the range of applications of superconductivity
- ii. Give five applications of low temperature phenomena.

## 7.0 REFERENCES/FURTHER READING

Adams, S. & Allday, J. (2000). *Advanced Physics*. Oxford University Press, UK.

Bueche, F. J. & Hecht, E. (2006). *College physics*. Schaum's Outline Series. New York: McGraw-Hill.

Cutnell, J. D. & Johnson, K. W. (1989). *Physics*. USA: John Wiley & Sons, Inc.

Gibbs, K (2011). *Advanced physics, 2<sup>nd</sup> ed*. Cambridge: Cambridge University Press.

Halliday, D., Resnick, R. & Walker, J. (2001). *Fundamentals of Physics-Extended (Sixth edition)*. New York: John Wiley and Sons, Inc..

Palmer, B. S. & Rogalski, M. S. (1996). *Advance University Physics*, Gordon and Breach Science Publisher SA.

Rao, Y. V. C. (2004). *An Introduction to Thermodynamics* (Revised Edition). India: University Press (India) Private Limited.

Sears, W. F. & Salinger, G. L. (1975). *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics* (Third Edition). Philippines Addison-Wesley Publishing Company, Inc..

Stroud, K. A. (1996). *Further Engineering Mathematics* (Third Edition). London: Macmillan Press Limited.

Vuille, C., Serway, R. A. & Faughn, J. S. (2009). *College physics, 8<sup>th</sup> ed*. Belmont, USA: Brooks/Cole.

Zemansky, M. W. & Dittmann, R. H. (1981). *Heat and Thermodynamics* (Sixth Edition). New York: McGraw-Hill Book Company.