Temperature; A thermodynamic concept and application

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Abstract— **This article is meant in recognition to the temperature as one of the five pillars (P, V, U, T, S) of thermodynamics. The historical development of the Cellini's temperature scale based on the zero law is introduced. The decrease in temperature of real gases due to free expansion or against external forces is discussed. This was followed up with application of low temperature in industries such as liquefaction of air and specifications of materials handling liquid gases are surveyed. In academic research, attempts to approach the absolute zero, and the behaviors of the nucleus of some metals in particular the super conductivity was mentioned. Contrary to the expectation super conductivity was realized.** *(Abstract)*

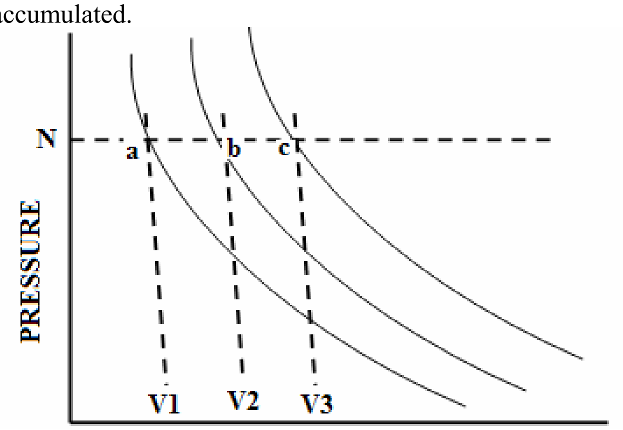
Keywords-Temperature; temperature; thermodynamic functions; state functions

I. INTRODUCTION

Cold and hot are two adjective words commonly used in describing the hotness and coldness of anybody. In our daily life we are familiar with phrases such as cold weather or very cold weather or worm water or hot air and so on. These two words (hot) and (cold) are translated into numbers that can be read on a thermometer instead of the words hot, cold, warm etc. we can read numbers like 80 or 50 or 100 or more or less. These numbers are defined by different scales. It is a great event to transfer from the era of sensation to the era of thermometers. For boiling water when we use our sensation by dipping our finger we say it is very hot, but when we dip a thermometer instead we read the number l00. The thermometer has become a scale on which we can read the degree of (hotness) and (coldness) which both are replaced by the word (temperature)[1-3].

The credit for the development of the temperature scale goes to the almost forgotten law; it is the ZEROTH LAW of thermodynamics. This law is based on thermal equilibrium between bodies (or systems) and it tells us in its one simple statement that when three bodies arranged in series A, B, C are in thermal contact with each other and when body (A) is in thermal equilibrium with body (B) and body (C) is in thermal equilibrium with body (B) then body (C) must be in thermal equilibrium with body (A)[1-3].

According to this law the three bodies which are in thermal equilibrium are at the same hotness and coldness. Suppose we have an ideal gas in a cylinder fitted with a weightless piston capable of moving up and down without any friction between the walls of the piston and the walls of the cylinder (ideal conditions). Let the gas be in thermal equilibrium with surrounding and does not exchange matter with it (closed system i.e. constant mass). The volume and the pressure of the gas may be varied while keeping the thermal equilibrium state between the gas and the surrounding (water bath) constant. A set of pressures and volumes data may be recorded at certain degree of hotness or coldness. If we change the hotness or coldness by heating the surrounding (water bath) or cooling it until thermal equilibrium is attained. Another set of P, V may be produced by varying pressure with volume a third or more attempts may be done and hence more P,V data are accumulated.



Volume
Figure-1

We ought to remember that up to now we have not referred to the word temperature. When these sets of P, V values are plotted as P versus T for various thermal equilibrium states we obtain several isothermal curves as shown in figure (1).

Let us take any point on the pressure axis, say point N and draw a parallel line to the volume axis. This line which is isobaric (constant pressure line) will intersect with the three curves in three different points. Each point resembles, certain volume on the volume axis as V_1, V_2, V_3…. V_n. From this plot we can realize a minimum volume V_1 obtained from curve (a), (cold surroundings) and a maximum volume V_3. obtained from curve (c) (hot surroundings). Let us put such findings into practice. Consider a capillary glass tube open from one end and with a round closed end bulb acting as a mercury reservoir. Mercury metal is introduced to fill the bulb and the lowest part of the capillary. The glass capillary tube bulb is dipped in water- ice mixture saturated with air under atmospheric pressure. The mercury will stay in position as long as the three phases (liquid water, water vapor and ice) are existed. It is known that the COLDNESS of the mixture will be fixed and will not change until one of the phases vanishes. For this reason the water vapor-ice mixture is taken as a reference for the coldness[1-3].

A scratch is made on the capillary glass tube indicating the position of mercury inside the capillary tube. This scratch is given the number zero (0. 0). It resembles the TRIPLE POINT of water. It never changes as long as it is in these three phases mixture. On the other hand when pure water is heated under atmospheric pressure, it boils with constant degree of HOTNESS. The capillary tube is then dipped in this boiling water. The mercury expands smoothly inside the capillary tube. It stops at a certain point and never changes its position as long as water is boiling under atmospheric pressure. Another scratch is made on the capillary glass tube marking the upper limit that mercury may expand under such conditions. This mark is given the number 100. It resembles the BOILING POINT of pure water. The distance between the zero (0.0) mark and the hundred (100.0) mark is equally divided into 100 divisions[1-3].

The end point of the capillary glass tube is sealed and thus A TEMPERATURE SCALE is developed. The symbol C is attached to the number. It represents the first letter of the name CELLICIUS the scientist who developed this temperature scale. The word temperature is a measure of the degree of COLDNESS and HOTNESS of any body. The zero degrees centigrade ($0^{\circ}C$) represent the freezing point of pure water under atmospheric pressure, while $100^{\circ}C$ represents the boiling point of pure water under atmospheric pressure. Other temperature scales are developed. The absolute ideal gas temperature scale commonly known as the KELVIN SCALE is the nearest to the CELLENIUS scale. in Kelvin scale the lowest temperature is taken as -273.15^{o} C which resemble the zero degree Kelvin K. Both scales are related to each other by simple relation $T\ K = T^{\circ}C + 273.15$. the $100^{\circ}C$ is easily converted to Kelvin scale by simply added to 273.15 to become 373.15 K and vice versa. This explains why the Cellini's temperature scale retained its position in the new SI system. It is not our intention to go into details to the different types of temperature scales but rather to go into details about the zero Kelvin (or the absolute zero), the temperature at which research are focused to approach but impossible to reach. The second law of thermodynamics has explained the reason behind it[1-3].

Temperature which is defined as a quantitative measure to the degree of hotness and coldness is one of the most important thermodynamic parameters. It is a property inherited in every species in this universe. In thermodynamics it is intensive property. The temperature must be specified for every physical or chemical thermodynamic measurement. Otherwise numerical values or Interpretations become obscure. As an example we mention, density, viscosity, conductivity, heat capacity, volume, pressure and other thermodynamic quantities and chemical reactions and we have to refer to the temperature at which these properties are measured. More over temperature makes with the other properties such as, the pressure (P) and the volume (V) a very important sets of variables that through which the ideal gas and the real gas equations of states are developed the functional relation $f(p,v,t) = 0$ is the base to the functions : $V = f(P,T)$, $P = f(V,T)$ and $T= f (P, V)$. from these functional relations we can derive more and most important thermodynamic terms and equations. The more important feature of these variables is that they are measured experimentally and their values are used to calculate the Gibbs free energy which cannot be measured experimentally, unfortunately, as it is always being agonized by thermodynamics scientists. These examples is presented to show the importance of temperature in thermodynamic studies [1-3].

TEMERATURE AND MODERN WORLD: Nowadays temperature concept is very much attached to the modern civilization. Scientific research has been directed towards both LOW TEMPERATURE and HIGH TEMERATURE production named as low temperature technology and high temperature technology.

High temperatures are needed in many aspects of life; Furnaces where temperature may go up to thousands degrees, steam power plants, vapor phase reactions are examples of high temperature production and application. In steam power plants the greater the steam temperature (super-heated steam) the greater the efficiency of the plant.

Going for a higher temperature as required by industry is not always feasible. It is cornered by engineering design where economics takes the priority. Going for high temperatures need equipment of high specification where as an example to resist corrosion and must be of high melting point this needs noble metals or special alloys both types are very costly and may be only used in some research laboratories. Transparent silica tubes can tolerate temperatures above thousand degrees centigrade and they are very expensive, the same goes with stainless steel, gold, silver, platinum, iridium and others. Optimum temperatures are always sought in the engineering design [1-3].

On the other side we have THE LOW TEMPERATURE PRODUCTION where refrigeration, air conditioning, gas liquefaction, surgical treatment are sample examples of so many on the application of low temperatures. . Even in the steam power plant, mentioned earlier, the lower the temperature of the condenser the higher the efficiency of the plant. And it reaches maximum efficiency at absolute zero, the temperature that is impossible to reach. However the temperature of the working fluid (tap water) of the condenser is the ambient temperature. It is therefore we are on the verge of two technologies; high temperature technology and low temperature technology.

In this article it is aimed to concentrate on the low temperature technology production and application.

The production of low temperatures stemmed its originality from the very early work of Joule in 1843where he for the first time tried to measure the effect of free expansion of a gas (expansion of a compressed gas into vacuum) on the internal energy of a gas which is referred to as (dU / dV). the experiment was carried out in a constant temperature bath in order to observe any change in temperature during this free expansion. By that time the experiment was crude enough, at least in the accuracy of the thermometer so that no change in temperature was noticed and hence Joule concluded that no change in internal energy occurred during that free expansion process. In other words dU = 0. 0. However this conclusion goes in harmony with the properties of the ideal gas which admits the existence of the molecules but considered its volume is so small that it has no effect on the volume it occupies. Besides there are no inter molecular forces (attraction and repulsion) among them. Therefore expansion of an ideal gas in vacuum or against any external force will not affect its internal energy neither does compression where heating effect (increasing in temperature) will never occur. This is justified by the first law du q — p d v. Since heat supplied to the system is zero (isolated system),and work done is also zero (expansion in vacuum), hence dU= 0. 0 -0. 0 = 0. 0 [1-3]

• Joule's experiments were repeated by other workers and showed that though very small, there is a decrease in temperature and hence there is a change in internal energy which is related to the volume change by the relation (dU / dV) which is named as Joule's coefficient and given the symbol (n). This change in temperature was attributed to the inter molecular forces between molecules a characteristic of what is named a REAL GAS or ACTUAL GAS. This attraction - repulsion forces are referred to as internal pressure. Since in this universe all gases are real gases therefore attention has been focused on the variation of temperature due to expansion with change in volume (dT / dV) at constant U. Such finding was confirmed by cooperative work between Joule and Thompson (lord Kelvin) whose experiment involved slow throttling of a gas at constant pressure through a rigid porous plug. The experiment was repeated at different pressures. Hence the throttling effect is related to a constant ENTHALPY rather than to a constant INTERNAL ENERGY. The new Joule- Thompson coefficient relates change in temperature to the change in pressure (dT/dP) at constant enthalpy. During their experiments Joule and Thompson had realized that sometimes they obtained a rise in temperature (heating effect) rather than cooling. And soon they realized that each gas has to be cooled in advance to a certain temperature and compressed to a certain pressure so that cooling will be obtained on throttling the gas. The temperature at which the gas responds to cooling is called INVERTION TEMPERATURE. Throttling means that a compressed gas is allowed to expand through an orifice (a very narrow opening). This cooling phenomenon has opened a new, area in the field of cooling technology the outcome of which is refrigeration, air conditioning, liquefaction of gases and research in low temperatures and its applications in various fields mainly in industry and medicine. Besides an academic research with aim to reaching the absolute zero Kelvin degree. Not only the Joule-Thompson throttling cooling effect was utilized, but also the adiabatic expansion method is also utilized for cooling gases and hence liquefaction is maintained. These two methods are utilized either individually or simultaneously. Work on the production of low temperatures are focused to achieve two purposes : a) industrial application, b) -academic application with the attention to 1) effect of low temperature on the behavior of nucleus of atoms of some metals such as rhodium, 2) -approaching the lowest temperature ever possible which is -237. 15°C the temperature which is impossible to reach.

II. DISCUSSION

A. *The Joule - Thompson Effect*

Thermodynamic analysis shows that free expansion of a compressed gas under an isolated conditions gives dU=O. This is because no work is done (W=0) and because the system is isolated, no heat entering or leaving the system, Q=O and since the first law says: dU = O-P dV therefore dU= 0. Such result is expected for an ideal gas but actually we deal with existing gases which we call actual or real gases characterized with inter-molecular forces. Free expansion of a gas or against external forces will be on the expense of these forces (attraction-repulsion forces). In this method under the given conditions of cooling to the inversion temperature and compressing to a certain pressure any gas may be liquefied. The gas to be liquefied is usually freed from impurities such as carbon dioxide and water vapor to prevent them from being solidified as in the air liquefaction the gas is then allowed to expand through a throttle or a valve. The throttled gas being now cooled is allowed to move upwards thus exchanging heat with the incoming gas through a heat exchanger. When this batch is throttled it has a better chance for a lower temperature than its predecessor batch. iteration of the process by compressing and throttling would lead to convert the gas to a liquid. Such a process is illustrated in figure (2) below. That is all can be said about the JOULE-THOMPSON cooling effect. Of course we have avoided to go into the details of the inversion temperature study which is discussed in thermodynamic and physical chemistry text books [1-3].

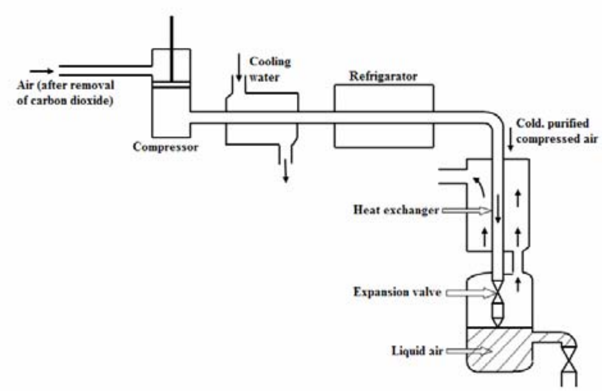


Figure-2 Liquefaction of air by Joule-Thompson cooling effect

B. *The Adiabatic Expansion Process*

In this process we achieve two objects; doing work and lowering the gas temperature. The gas (or air) is usually compressed to about 40 atmospheres and was allowed to expand to 1 atmospheres in an expansion engine where external work is done which is utilized to drive a dynamo. The expanded air is eventually cooled and on leaving, it will exchange heat with the incoming batch of air. then it will be compressed and re expanded again. Continuous compression and expansion will serve the two purposes, driving the dynamo and cooling the air until liquefaction occurs. Claude in his modified process used pressure up to 2000 atmospheres thus securing a great pressure difference and hence obtaining lower temperatures good enough to bring air to the liquid state. However the difference in temperature is proportional to the difference in pressure. W. Hampson in 1895 started his experiment with 200 atm. expanding to 1 atm. At the same year Von Linde used a compressed gas allowing it to expand to 40 atm. The temperature at which the first drop of liquid formed is called the condensation or the boiling temperature, or if it is air consisting of a mixture of gases it is called the dew point. At this point we have two phases at equilibrium; the liquid phase and the vapor phase. Our interest is to keep compressing and allowing expansion until complete liquefaction is obtained. Temperatures below the boiling points were attained by evaporation of liquid gases under reduced pressures. By this method liquid sulfur dioxide was cooled to (- 65°C) and solid carbon dioxide (dry ice) is produced by quick evaporation[4]. On industrial scale for liquefaction of air both methods the Joule- Thompson and the adiabatic methods are used at the same time. In this sense the compressed gas may be divided into two streams; one stream flows through a heat exchanger thus cooling the incoming gas while the other stream is directed to expand adiabatically against an external force thus producing work. Ever since of the discovery of cooling to lower temperatures great efforts have been put to invest this phenomena into practical use. One of the earliest methods was to solidify, carbon dioxide which was utilized by R. P. Pietit in 1877 for the liquefaction of oxygen. That was the beginning of putting the low temperature processes into industrial application. . Liquefaction of air represent the first and the most important industrial process. From this process it was possible to separate oxygen from nitrogen by fractional distillation since both have different boiling points. Liquid oxygen boils at -183°C and liquid nitrogen boils at -195°C . The difference in boiling temperatures make nitrogen boils first while oxygen remains in its liquid state. However after separation gaseous nitrogen at its boiling temperature -195°C can be compressed at the same temperature (reversibly) to the liquid phase. Practically compression is accompanied with slight increase in temperature. Therefore the Joule-Thompson process is practiced for this purpose. Hydrogen gas was also liquefied at -253°C, and liquid helium at -269°C [5].

Liquefaction of air and other gases has the advantage of both easy storing as liquids and hence easy handling. However liquid oxygen, nitrogen, helium and other gases may be evaporated and compressed in cylinders marketed to laboratories and other industrial establishments. Methane gas making the main component in natural gas has a boiling point of -162°C and is transported as liquid in well insulated ships.

C. Third method used in bringing the temperature toward the zero Kelvin is the ADIABATIC DEMGNETZATION method.

Temperature as low as 1K was reached by joule -Thompson evaporation process where liquid helium is vaporized by pumping through pipes of large diameters to confine the huge amount of helium used in this process. However the demagnetization is used for temperatures below 1°K. In this method one has to realize some concepts such as magnetic field, para magnetism, and diamagnetism spinning of an electron, spinning of the nucleus, etc. Along with that two important thermodynamic parameters Energy and Entropy have to be considered. All these concepts are related to each other's to attain the lowest possible temperature. As we know there is a direct relation between temperature and entropy. Also Temperature is related to the thermal energy. Also Therefore the adiabatic demagnetization process is used to extract the last traces of thermal energy from the crystal lattice via the electron spin and nucleus spin and throwing it into liquid helium which acts as the surrounding. Total change in entropy is equal to zero (adiabatic process), and hence a decrease in entropy of the crystal is balanced by an increase in entropy of liquid helium making the total change in entropy equal to zero. The adiabatic demagnetization is carried out reversibly. To relate the temperature to the entropy we have to point out that contribution to entropy comes from three sources thermal energy(heat energy), potential energy due to the position of electrons above the datum level (the nucleus) and the uniformity of molecular distribution in the crystal lattice. For example the arrangement of carbon monoxide molecules in the crystal lattice may be either COCOCOCOCOCOCOCO which makes a perfect crystal or COCOCOOCOCCOCOOCOC which makes imperfect crystal. In this last structure the molecules are randomly distributed and is considered as a mixed crystal and has a definite value of entropy. This comes from the fact that when two gases at the same temperature are mixed but with different volumes and pressures there will be an Increase in entropy.[7] What we are trying to get at is that can we reach the zero Kelvin if all thermal energy were extracted but there remains the spinning electron and nucleus entropy? And along with that the imperfectness of the crystal lattice. The answer to this question is already known. Reaching the zero absolute temperature needs complete cease to all types of particle motion,. In other words molecules have to reach a quantum mechanical effect called zero-point energy. Quantum mechanics does not allow reaching such a state. It is also known that no adiabatic process can lead in finite steps to zero absolute. In conclusion reaching absolute zero is impossible. Although Helsinki University of Technology reported a temperature of 100 PK (0.1^{10}) and in 2003 research at MIT achieved 500 PK (0.5^{10}) research is continued toward the absolute zero just to achieve a record. This very low temperature approach has in fact opened a new area in scientific research. for example this cooling effect was done on a piece of rhodium atom with purpose of achieving lower temperature and to study the magnetism of the nuclei of the rhodium atoms. The researchers hoped to freeze the moments of the nuclei but contrary to their expectation the rhodium nuclear moments did not freeze even at 10 raised to minus ten of a degree. To their surprise shows super conductivity. The researchers were able to study how nuclear magnetism affects the super conducting electrons. Low temperatures found its application in various fields. One of these fields is engineering materials. In this respect the liquefied natural gas (LNG) imposed a certain restrictions on equipment and materials used to handle it. Since the temperature at which LNG becomes liquid ranges from -150^{o}C to -182^{o}C then the type of materials of construction have to be carefully selected. For example mild steels become extremely brittle at about (-50°C). Thus they cannot be of use for construction of equipment carrying LNG. To satisfy that low temperature range materials whose ductility suffer no change when in contact with low temperature liquids such materials are called nil ductility transition (NDT). Such materials can withstand low temperatures below -160^{o}C. An example of these materials are nickel, copper, most of aluminum alloys and many high nickel/ chromium stainless steels. Such steels are rather expensive but there are some steel alloys are cheaper and at the same time meets the American standard testing materials (ASTM) specifications. among them are 5% and most of 9% nickel steels. In the design of cryogenic equipment consideration must be taken to the large dimensional change due to the change in temperature from ambient temperature to the cryogenic temperature. Examples of such equipment are pipes, storage tanks, pumps and every single part of equipment in direct contact with cryogenic liquid. It is stated that 9% Ni steel is the only ferrite steel which is permitted for use at liquid nitrogen temperature (-196^{o}C). It is also economical for the construction of storage tanks for liquid argon(-183°C) and methane (-161°C).

Ethylene oxide abbreviated as EO is stored at a low temperature between (-6.6 and -20.65°C). Such a refrigeration storage has several advantages. It decreases the rate of its polymerization and may help precipitation of the already formed ethylene oxide polymer. Also refrigeration helps removal of heat that is formed due to contamination totally or most of it, thus putting such possible reactants under control. Ethylene oxide storage under such a low temperature will avoid possible explosion due to the presence of its vapor in the top region of the storage tank. Low temperatures have found wide applications in medical field. A summary of these applications and other academic applications may be readily approached through the internet[8].

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