

# Absolute Temperature

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## ABSTRACT

Absolute temperature or minimum possible temperature universally accepted by scientific community is about  $-273.15^{\circ}\text{C}$  or 0 kelvin. At the end of 18<sup>th</sup> century and beginning of 19<sup>th</sup> century, Charles and Lussac experimented with behavior of gases and found direct and linear relationship between temperature and volume of gases at constant pressure. The V-T curve plotted were straight lines obtained by experimental data between  $27^{\circ}\text{C}$  and higher temperatures. The V-T line was extrapolated in lower temperature region below  $27^{\circ}\text{C}$  and extended till the line touched volume axis, where volume becomes 0. It touched temperature line at about  $-273^{\circ}\text{C}$ . It was believed that volume can not be less than 0 and thus it was found that  $-273^{\circ}\text{C}$  is the minimum possible temperature or absolute temperature. Thus a theoretical lower limit of  $-273^{\circ}\text{C}$  was set for temperature. But in all practicability, volume of a gas can not be 0 as molecules will occupy some space even at minimum temperature and V-T line can not touch temperature axis. Secondly, it violates conservation of mass since 0 volume implies 0 mass. So yet not measured, temperature can assume any lower value theoretically. Pressure and temperature of gases also have linear relationship at constant volume. P-T lines of different gases when extrapolated in lower temperature region also converged at  $-273^{\circ}\text{C}$ . It was also believed that pressure too can not be less than 0 and this further ratified the value of minimum possible temperature. But there is another possibility that at 0 pressure gas is in a state of contraction and its molecules have translation (above its zero point energy) in contracted volume due to high inter-molecular forces at very low temperatures. The present assessment of absolute temperature is based on study of gases which have translational degree of freedom at very low temperature. Molecules of solids in contrast have vibrational degree of freedom. Low temperature study of degrees of freedom of solid molecules and its properties might be more helpful in study of absolute temperature. Debye model of specific heat predicts dependence of specific heat with cube of temperature, which means for large change in temperature there is a small change in specific heat. Further Einstein-Debye model of specific heat established presence of electron specific heat in metals such as copper at very low temperature. Electron specific heat of superconducting materials in superconducting state is found to be yet lower than electron specific heat in normal state below their transition temperature. Electrons participation in specific heat and specific heat-temperature curves of solids may bring new facts about absolute temperature.

**Index Terms** - Absolute temperature, Minimum possible temperature, V-T plot of perfect gases, Electron specific heat, BCS theory of superconductors, P-T plot of perfect gases.

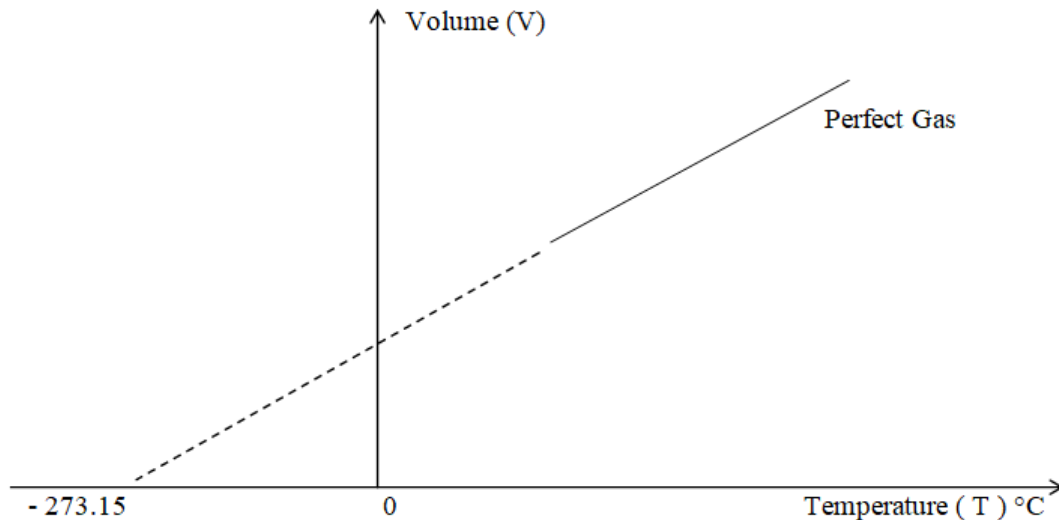
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## INTRODUCTION - CONCEPT OF ABSOLUTE TEMPERATURE

### Volume – Temperature curve of perfect gases

Jacques Charles (1787) and Gay Lussac (1802) made detailed experiments on how the volume and pressure of a gas was affected by the temperature of the gas. Jacques Charles kept all properties of the gas constant, except for temperature and volume. It was observed that the volume of a gas increases linearly when the temperature rises and conversely the volume decreases when the temperature drops. Experiments were done in temperature range of standard temperature ( $27^{\circ}\text{C}$  centigrade) and above.

The observations were plotted on graph with volume as Y-axis and temperature as X - axis. A linear relationship was observed between temperature and volume of a gas. Observations were extrapolated in range of low temperature rather than finding of empirical values. The V-T line was extended till the volume became zero (shown as dashed line). It was thought that the temperature corresponding to zero volume was the minimum possible temperature since the volume of a gas becomes zero at this temperature and further the volume can not be negative.



These experiments and assumptions were made much before the theory of relativity and the much famous energy mass equation  $E=mc^2$  was derived by scientist Albert Einstein (1905). Certain assumptions were made about perfect gas but it's certainly established that a mole of perfect gas will have  $N_A$  (=Avagrado number) molecules. A molecule has a certain mass. It can not be assumed that a molecule is massless. The energy mass equation predicts that energy and mass are inter convertible and a large amount of energy is liberated when a small mass is converted into energy. Other fact observed about the behavior of gases is that the density of a gas increases when the temperature is decreased. Density is ratio of mass and volume of a substance . It can also be written as

$$\text{Mass} = \text{Density} \times \text{Volume}$$

As the volume decreases linearly when temperature is decreased, the density increases so that the mass remains constant. The relationship also implies that if volume=0, then mass=0. So assuming that volume of a perfect gas becomes zero at absolute temperature is against law of conservation of mass firstly. And moreover if mass is lost in process, equivalent amount of energy must be libereted according to energy mass equation which is extremely large even for a small mass loss because of large value of velocity of light. In the light of above two simple and universally accepted facts, It is postulated that the temperature -volume line can never touch the X- axis in contrast to belief of Charles and Gay Lussac and also the volume of a gas can not be zero at absolute zero temperature as concluded by the above cited scientists. So, it can not be definitely established that absolute temperature (or minimum possible temperature) is  $-273.15^\circ\text{C}$  (or point of intersection of V-T line and temperature axis corresponding to 0 volume).

Energy liberated by a mass of 1.12 Kg according to energy-mass equation  $E=mc^2$  will be ,

$$= 1.12 \text{ kg} \times (3 \times 10^8)^2 \text{ meter}^2 / \text{second}^2$$

$$= 10^{14} \text{ Kilo Joules}$$

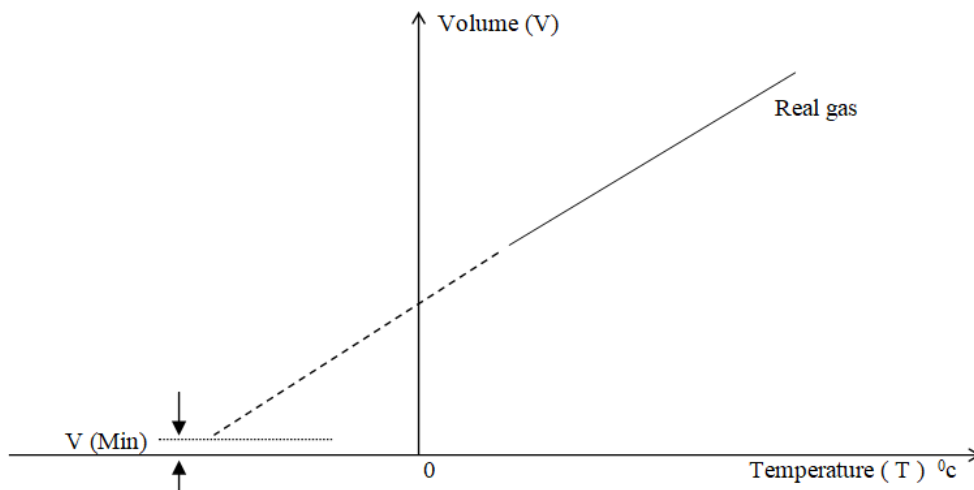
This large amount of energy liberated is capable of raising the temperature of 1.12 Kg of air at normal temperature by  $9 \times 10^{13}$  degrees. If specific heat of air at constant pressure at  $27^\circ$  celsius is taken as 1 k Joule/kg K then  $10^{14}$  kilo joules of energy will raise the temperature of 1.12 Kg of Air by

$$\Delta T = \frac{Q}{\text{Mass} \times \text{Specific Heat of Air}}$$

$$= \frac{10^{14} \text{ kilo joules}}{1.12 \text{ kg} \times 1.0 \text{ kilo joule / kg k}}$$

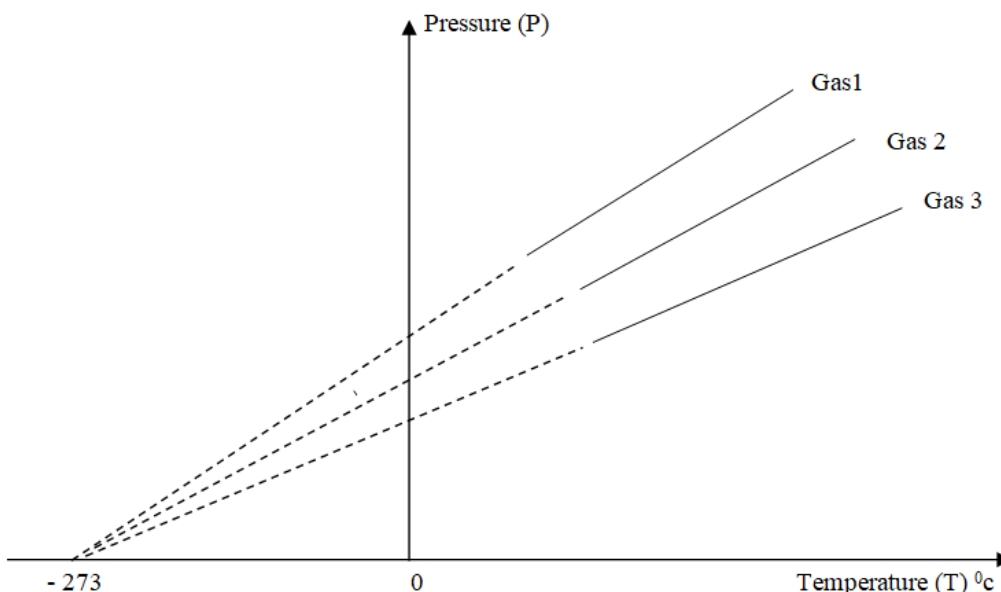
$$= 9 \times 10^{13} \text{ k}$$

This rise in temperature can not be ignored nor the energy liberated can be ignored. it is also concluded that at minimum possible temperature ( or absolute temperature), the V-T Line will not touch the temperature axis at any point, But will find an abrupt end as shown in the figure below. The abrupt end will correspond to the minimum volume which a gas will occupy. This cancels the theoretical limit of  $-273.15^\circ\text{C}$  imposed upon temperature as its lower limit and yet not experienced but temperature can assume any lower value.



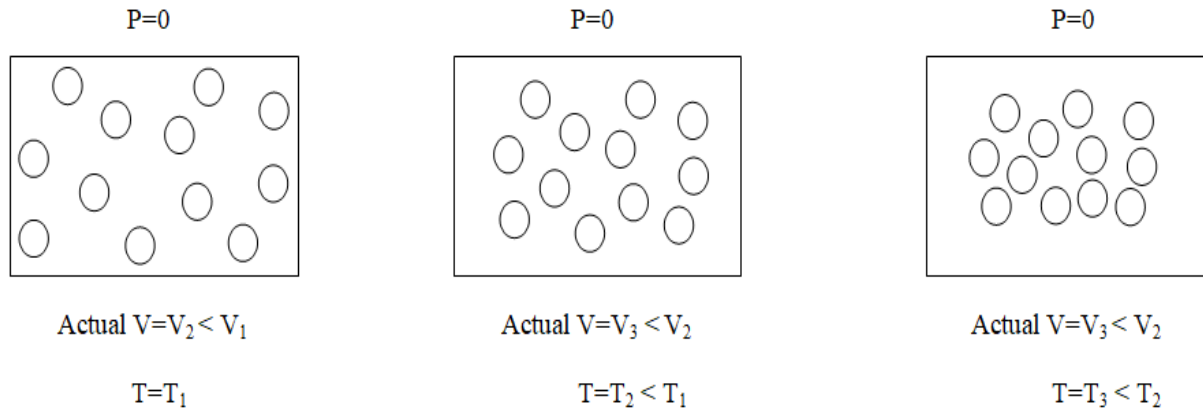
**Pressure – Temperature curve of perfect gases**

Perfect gases follow linear relationship between its pressure and absolute temperature when volume is kept constant. Different gases obey a different linear relationship of pressure and temperature and are represented by a distinct line on P-T axis. But it has been observed that the pressure of all the gases become zero at about  $-273\text{ }^{\circ}\text{C}$  (or 0 Kelvin) and meet the temperature axis near this point when the lines obtained by experimental values are extended leftwards. The dashed lines are extrapolated part whereas full lines are obtained by empirical values. It was assumed that further lowering of pressure is not possible as pressure as a physical quantity can not be less than zero. So it was assumed that where P-T curves of gases intersect the temperature axis should be the minimum possible temperature. This was also verified by analysing distribution and variance using Krushal and Wallis test on data of several gases obtained experimentally. Predicted absolute temperature where pressure becomes zero by Krushal and Wallis test also matches close to  $-273\text{ }^{\circ}\text{C}$  as obtained by V-T lines of gases.



Zero pressure is a state, achieved when molecules of a gas have not enough kinetic energy to strike on the walls of container and thereby are unable to exert a pressure on it, which can be sensed. Any sensor will read zero pressure in the situation. But it will be preposterous to assume that it is the state of minimum kinetic energy associated with translational motion (above zero point energy) of gas molecules. Thus, this state does not imply that minimum temperature condition has been achieved.

If it is assumed that state of minimum temperature has not been reached despite zero pressure being sensed at the container walls, the gas molecules must have degree of freedom, so that transferrable thermal kinetic energy can be stored. When temperature of a gas is reduced, inter molecular spacing is also reduced resulting in stronger intermolecular forces. At extremely low temperatures a perfect gas (supposing it will not liquify) hypothetically assumes a state of contraction. The actual volume and amplitude of translation keep reducing but molecules still have translational degree of freedom (above zero point energy) as modelled below.



Perfect gas in contracting state at 0 pressure

### SPECIFIC HEAT OF SOLIDS AND ABSOLUTE TEMPERATURE

#### Degree of freedom and Temperature

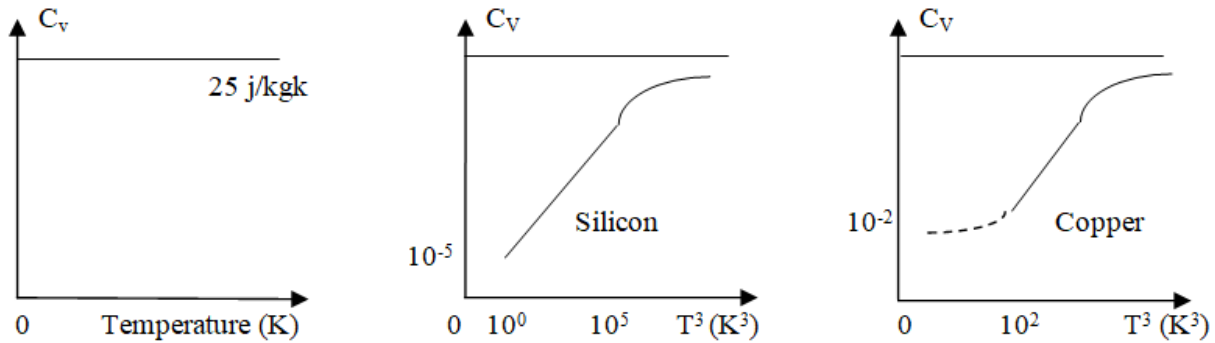
Temperature microscopically, is in essence measure of kinetic energy of constituent micro particles of a system. Kinetic energy of molecules is directly associated with degrees of freedom (or number of unique ways molecules can have motion as translation, rotation and vibration). Molecular degrees of freedom decide how kinetic energy is stored and distributed in molecules. Equipartition (of energy) law states that when thermal energy is added to system it is shared equally among degrees of freedom. Each degree of freedom contributes equally to total energy of system and on average has energy equal to  $\frac{1}{2} KT$ . Moreover each degree of freedom contributes equally in specific heat of system amounting  $\frac{1}{2} K$  where  $K$  is boltzmaan constant and  $T$  is absolute temperature.

An atom or molecule of a noble gas can have translational motion along 3 axes of cartesian coordinates and hence have three degrees of freedom associated with translation. Atoms have negligible rotational energy since mass is centered about nucleus. But linear molecules have two degrees of freedom and non linear molecules have three degrees of freedom associated with rotational motion. Rotational degree of freedom will contribute to energy of a gaseous system above temperature of 30 K and at temperature below this, it is insignificant and does not contribute in energy or specific heat of system. Particles can have vibrational motion also. A diatomic molecule has one vibrational mode. A linear molecule with  $N$  atoms has  $(3N - 5)$  vibrational mode and a non linear molecule has  $(3N - 6)$  modes of vibration. Each vibrational mode has two degrees of freedom for energy ( it is similar to spring which has kinetic and potential energy components in total energy). It is approximated that vibrational mode contributes in specific heat of a gas only if the temperature is above 3400 K. Atoms of solids are bound by strong force and have no translational or rotational degree of freedom but they have vibrational modes of motion.

#### Specific heat of solids and Dulong and Petit law

Dulong and petit law states that the product of specific heat and atomic mass (gram atomic heat capacity) of elements is always a constant. It is applicable for solids and the product is constant( 6.4 cal/mole K or 25 Joule/mole K ) for all solid elements. The law is in confirmity with Equipartion law. Thermal energy added to solids is absorbed in form of atomic vibration. There are three vibrational modes and each vibrational mode has two degrees of freedom and stores energy equal to  $KT$  in each mode. Solid molecules can vibrate along 3 axes and energy of each molecule is  $3KT$ . Energy per mole of solid will be  $3KT N_A$  ( $N_A$  is Avogrado number ). Specific heat at constant volume ( $C_V$ ) per mole is temperature derivative of energy per mole and is  $3KN_A$  ( 25 joule/mole k). Since  $K$  and  $N_A$  both are constants and not element specific, it is constant for all solids.

This is Dulong and Petit law. The law holds good at high temperatures and  $C_V - T$  curve is a straight line corresponding to  $C_V = 25$  joule/kg-K. But at low temperatures specific heats drastically depart and show temperature dependence. Einstein and Debye developed models to explain the departure from Dulong and Petit law. Debye expressed specific heat of solids as a function of cube of absolute temperature ( $T^3$ ) such as  $C_V = aT^3$  where  $a$  is a constant. Debye's cube of temperature dependence model could explain departure from Dulong and Petit law for silicon at lower temperature but could not explain departure at low temperature for copper as shown in figure below. At high temperatures specific heat of silicon approaches Dulong-Petit specific heat but at lower temperatures it shows temperature dependence and matches with Debye's  $T^3$  model. Dulong and Petit law is based on Maxwell-Boltzmaan statistics and Equipartion Law. Its departure at lower temperatures implied that quantum mechanics must be used instead of classical Boltzmaan statitics.



$T^3$  dependence of specific heat of silicon and copper

### Einstein's specific heat model

Einstein used quantum mechanics to explain the departure of specific heat from Dulong and Petit's law. Einstein found that for quantum harmonic oscillator at energies less than  $KT$ , Einstein-Bose statistics must be applied which is quantum statistics of indistinguishable particles with spin 0, 1, 2, 3... (as in case of black body radiation). The average energy (of particles) found in statistical distribution of energy in vibrational states is given by

$$E_{average} = \frac{h\nu}{\left(e^{\frac{h\nu}{KT}} - 1\right)}, \text{ where } \nu \text{ is frequency of quantum vibrator.}$$

There are 3 modes of vibration, therefore total energy per mole is

$$E = \frac{3h\nu N_A}{\left(e^{\frac{h\nu}{KT}} - 1\right)} \text{ mole}^{-1}$$

and specific heat as temperature derivative of energy per mole is

$$C_V = \frac{dE}{dT} = \frac{3N_A K \left(\frac{h\nu}{KT}\right)^2 e^{\frac{h\nu}{KT}}}{\left(e^{\frac{h\nu}{KT}} - 1\right)} \text{ mole}^{-1}$$

The above Einstein expression for specific heat approached Dulong and Petit specific heat per mole  $3N_A K$  at high temperatures and Dulong and Petit law is higher limit of this expression. At large temperatures quantity

$$e^{\frac{h\nu}{KT}} = 1 + \frac{h\nu}{KT} \text{ substituting this in above expression of } C_V, \text{ we get}$$

$$C_V = \frac{dE}{dT} = \frac{3N_A K \left(\frac{h\nu}{KT}\right)^2 \left(1 + \frac{h\nu}{KT}\right)}{\left(\frac{h\nu}{KT}\right)^2} \text{ mole}^{-1}$$

$$C_V = 3N_A K \left(1 + \frac{h\nu}{KT}\right) \text{ mole}^{-1}$$

Neglecting  $\frac{h\nu}{KT}$  at high temperatures, Einstein expression reduces to  $C_V = 3N_A k \text{ mole}^{-1}$  as Dulong and Petit law. Einstein value of specific heat in general matched values with experimental values but still was not exact. Debye further modified it by treating quantum oscillator as collective modes in solid called phonons.

### Debye's specific heat model

Debye recognised that there was a maximum number of modes of vibration in solids and he presented at first the vibration of standing wave modes in the crystal. Debye arrived a maximum allowed phonon frequency called Debye frequency  $\nu_D$  and defined a Debye temperature  $T_D$  such that

$$T_D = \frac{h\nu_D}{K}$$

At low temperatures Debye found specific heat  $C_V$  equal to

$$C_V = \frac{12}{5} \pi^4 N_A K \left(\frac{T}{T_D}\right)^3$$

The dependence upon cube of temperature agreed with experimental results of non metals (silicon) but it did not match with experimental results of metals (copper).

### Electron contribution to specific heat

Electrons in metal that contribute to conduction are close to the fermi level ( 7ev for copper ). In order to contribute to bulk specific heat, all valence electrons should receive energy from nominal thermal energy  $KT$  ( $KT= 0.026$  ev at 300K). Since  $KT$  is much less than fermi level, there are few electrons to receive energy within  $KT$  and majority of electrons can not. But small number of electrons which are within  $KT$  of fermi level contribute a small specific heat which becomes significant at very low temperature. Contrary to Einstein -Bose model of phonons using Fermi-Dirac statistics, it is observed that a small number of electrons share a part into specific heat. Electron contribution is important only at very low temperatures in metal when it becomes large compared to  $T^3$  dependent phonon contribution. Electron specific heat is expressed as

$$C_V = \frac{\pi^2 N_A K^2 T}{2 E_f} \text{ mole}^{-1}, \quad \text{where } E_f \text{ is fermi energy.}$$

Debye's Phonon model as discussed above with its cubic dependence on temperature could agree with experimental data of silicon specific heat at very low temperatures but experimental data of specific heat of copper show departure from cubic dependence of temperature. The inclusion of electron contribution of specific heat could match with experimental data of copper.

### Einstein - Debye specific heat

Low temperature specific heat of metals could be explained by including electron specific heat contribution with phonon contribution. The combined specific heat expression arrived was

$$\begin{aligned} C &= C_{Electronic} + C_{Vibrational} \\ &= \frac{\pi^2 N_A K^2}{2 E_f} T + \frac{12 \pi^4 N_A K}{5 T_D^3} T^3 \end{aligned}$$

Debye's specific heat model with cube of temperature relationship was successful in explaining silicon specific heat till very low temperatures but copper specific heat curve deviated from Debye's model at very low temperatures. The copper specific heat curve, which flattens while approaching very low temperatures unlike silicon which is linear, could be explained by including participation of electrons in specific heat as above equation modelled by Einstein-Debye. Flattened copper specific heat -  $T^3$  curve at very low temperatures indicates that for a large temperature fall there is comparatively very small fall in specific heat while both tend to 0. The specific heat of superconducting materials in superconducting state is found to be, yet lower than specific heat in their normal state below transient temperature. Electron participation in specific heat suggest that thermal energy is possessed by electrons too. Absolute temperature has been established from the behaviour of real gases. At low temperatures only translational degree of freedom is significant in gaseous state. Absolute temperature may also be investigated by understanding behaviour of solids at very low temperatures, in which case vibrational mode is of importance. In understanding of absolute temperature, electron specific heat and specific heat-  $f$  (temperature) curve of solids could also be helpful.

## SUPER CONDUCTIVITY (SUPERFLUIDITY) AND ABSOLUTE TEMPERATURE

Many matter show a superconducting property below a temperature called Transient temperature. The specific heat of a matter in its superconducting state is less than that of specific heat in its normal state below this transient temperature. Transient temperature of various known superconductors have transient temperature between 0K to 10k with tungston having lowest transient temperature 0.015 K and niobium having highest transient temperature 9.2 K. According to BCS theory, superconductivity is due to electron pairing. Electrons normally repel each other since they have same polarity, but in superconducting state of matter they form a pair and navigate through the material with zero electrical resistance. The hypothesis to explain pairing of electrons is that valence electrons get closer to the phonon at very low temperature and becomes relatively positive charged compared to free electrons and thus the pairing results. But electron is quantum of charge and a charge say, equal to half of electron or a charge less than electron charge is not possible in present science. Other salient feature of the hypothesis was that free electrons behave like bosons and unlike fermions many bosons can be in same energy state. Further reason for electron pairing is that at low temperature they condense and can move in pair. Most important observation is that behaviour of superconducting (solid) materials change at their respective transient temperature just near 0 K temperature.

It is not unexpected that near 0 K temperature, behavior of gaseous state may also be unexpected for some cases. Natural Helium which is essentially  $^4\text{He}$  under normal pressure and temperature is a gas. It liquifies at 4k and

remains liquid at 0K below pressure 2.5 Mpa. When Cooled further below 4K, it transforms into superfluid at temperature near 2K when its viscosity is near zero and it can flow without resistance.  $^3\text{He}$  another stable isotope of helium transforms into superfluid phase at temperature 2 Millikelvin,  $1/1000^{\text{th}}$  of temperature at which Natural helium transforms. Superconductivity and superfluidity are interrelated and superconductivity is special case of superfluidity of electrons.  $^4\text{He}$  atom is a boson with integer spin and superfluidity of  $^4\text{He}$  is due to Einstein-bose condensation of helium atoms.  $^3\text{He}$  atom is fermion since it has  $1/2$  spin and its normal state is fermi liquid. Superfluidity of  $^3\text{He}$  is due to Cooper pairing of fermion systems. Superconductivity results when pairing of free electrons (net negative charge) occur and superfluidity is resultant of pairing of atoms (net charge zero) or pairing of electrons and positive holes (net charge zero) and both phenomenon have similarity of mechanism.

### CONCLUSIONS

Volume of a perfect Gas is not 0 at absolute zero temperature. Since V-T curve of a gas can not intersect temperature axis at any point, the theoretical limit of  $-273.15^\circ\text{C}$  imposed upon temperature as its lower limit is not valid. It may also be possible that at 0 pressure gas molecules have translation (above its zero point energy) in contracted volume due to high inter-molecular forces at very low temperatures. Yet not experienced, but temperature can assume further any lower value theoretically. So for assumption of absolute temperature is based on study of gases, which have translational degree of freedom at very low temperature. Molecules of solids in contrast have vibrational degree of freedom. Low temperature study of degree of freedoms of solid molecules and its properties, especially specific heat might be more helpful in study of absolute temperature. Debye model of specific heat predicts dependence of specific heat with cube of temperature, which means for large change in temperature there is a relatively small change in specific heat while both tend to 0. Thermal energy is possessed by electrons too, which is significant at very low temperatures as verified in Einstein - Debye specific heat model. In understanding of absolute temperature, electron specific heat and specific heat- f(temperature) curve of solids could also be helpful. Behaviour of many solid materials change at their respective transient temperature, which lies between 0K to 10K just near 0 K temperature and they transform to superconducting state from normal state. It is not abnormal that behaviour of gases be unexpected near 0K temperature and more investigations are required. Helium which is gas at normal temperature and pressure liquifies at temperature 4 K which is very close to 0 K and remain liquid at close proximity of 0 K under pressure 2.5 Mpa. Liquid state is not the minimum energy state and normally liquids solidify at lower temperature by losing some kinetic energy.

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