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Review Article

A Review on Absolute Temperature

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ABSTRACT

In this paper, we detail William Thomson's (Lord Kelvin) contributions to the theory of absolute temperature, which form the basis for the most exact temperature measurements performed today. Instead of counting temperatures from zero, Thomson's primary goal in developing his ideas of "absolute" temperature was to ensure that the term was defined in a way that was not dependent on the characteristics of any one thermometric substance.

1. Introduction

❖ Concept of Absolute Temperature

1. 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 degree centigrade) and above [1-5]. The observations were plotted on graph with volume as X-axis and temperature as Y- Axis. A linear relationship was observed between temperature and volume of a gas.

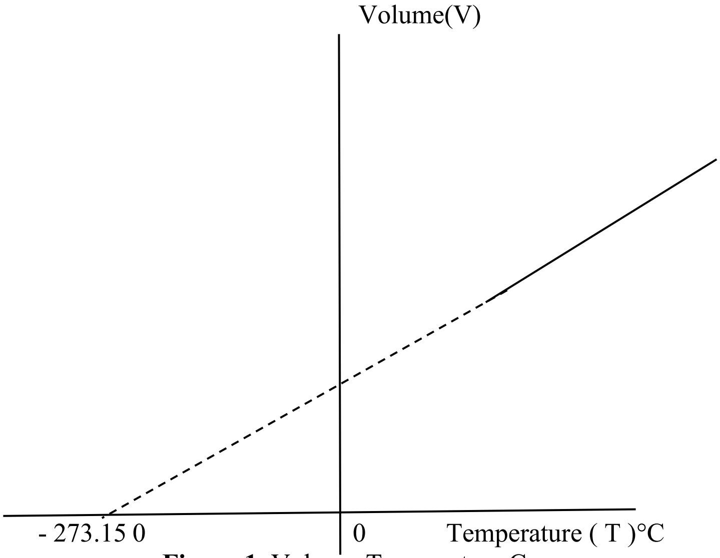


Figure 1. Volume-Temparature Curve

Observations were extrapolated in range of low temperature rather than finding empirical values. The V-T line was extended till the Volume became zero as shown as dashed line in fig 1. 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 cannot 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 cannot be assumed that a molecule is massless [6-10]. 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 [11-15]. 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 equation 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 liberated 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 cannot be zero at absolute zero temperature as concluded by the above cited scientists. So, it cannot be definitely decided that absolute temperature (or minimum possible temperature) is -273.15 °C (or point of intersection of V-T plot 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 × 10^{13} degrees. If specific heat of air at constant pressure at 27° 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

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

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

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

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 breaks the limit of -273.15 °C imposed upon temperature as its lower limit and yet not experienced but temperature can assume any lower value as shown in figure 2.

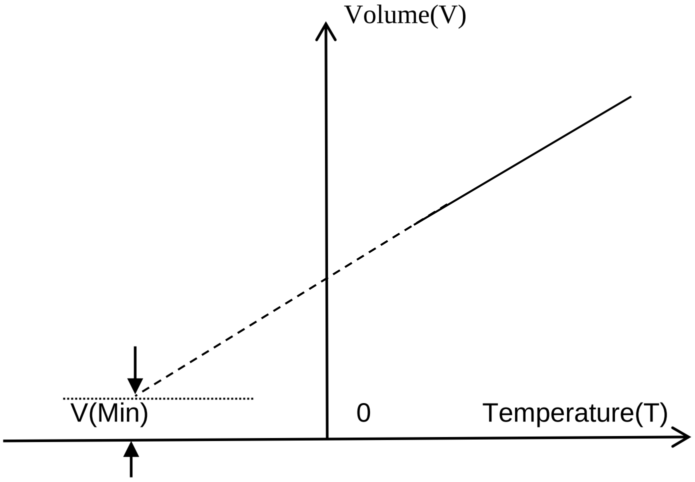


Figure 2. V-T Line

2. 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 curve. But it has been observed that the pressure of all the gases become zero at about -273 °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 cannot 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°C as obtained by V-T curve of gases.

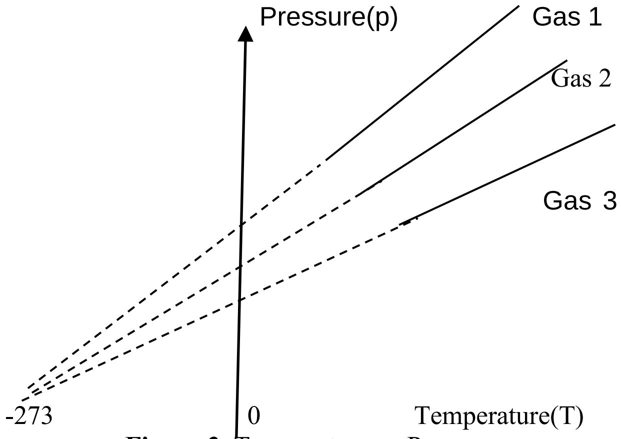
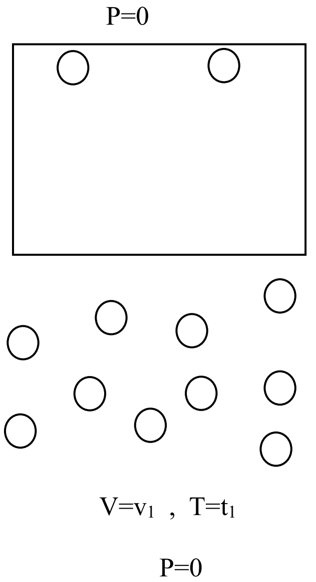


Figure 3. Temperature vs Pressure

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 exherting 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 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 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 as modelled below in fig 3.



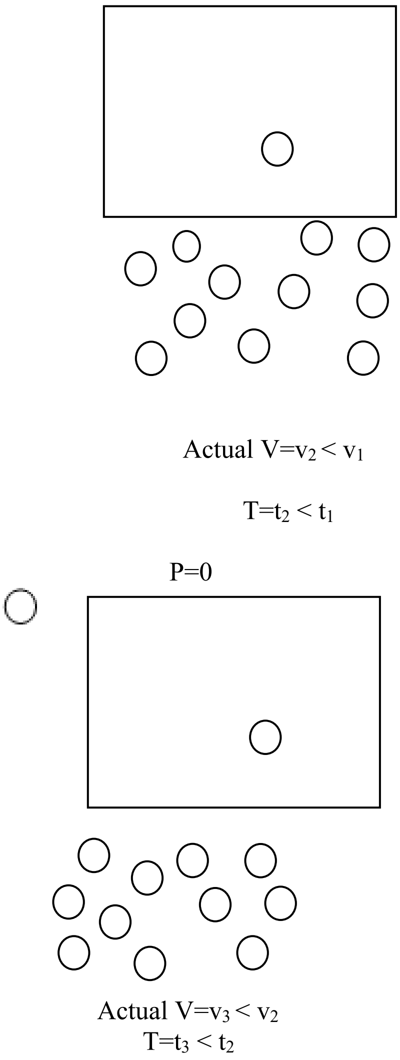


Figure 3. Presure vs Various Temperature conditions

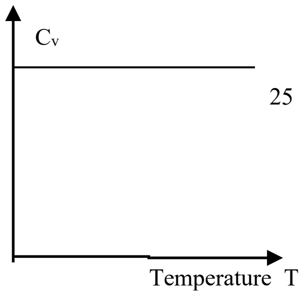
3. Degree of freedom and Temperature

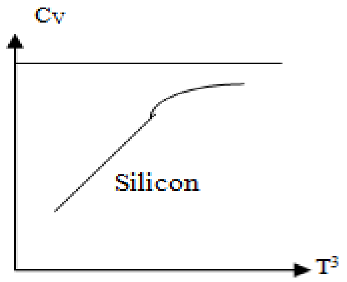
Temperature microscopically, is in essence measure of kinetic energy of constituent micro particles of a system. Kinetic energy of molecules is directly associated with degrees of freedom (or number of unique ways molecules can have motion as translation, rotation and vibration). Molecular degrees of freedom decide how kinetic energy is stored and distributed in molecules. Equipartion (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 ½ KT. Moreover, each degree of freedom contributes equally in specific heat of system amounting ½ 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 cantered about nucleus. But linear molecules have two degrees of freedom and nonlinear molecules have three degrees of freedom associated with rotational motion. 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). 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. 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.

4. Specific heat of solids and Dulong and Petit law

Dulong and petit law states that 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 3 KTN_A (N_A is Avogrado number). Specific heat at constant volume (C_V) per mole is temperature derivative of energy per mole and is 3 KN_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 in figure 4 is a straight line corresponding to C_V=25. 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.





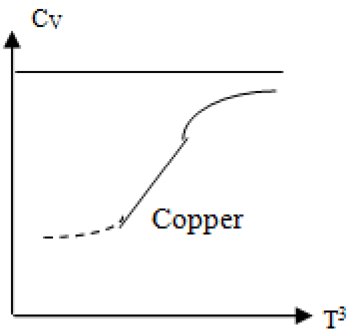


Figure 4. Cv-T Curve

Debye expressed specific heat of solids as a function of cube of temperature (T^3) such as $C_V = aT^3$. Debye model could explain departure from Dulong and Petit law to some extent but could not explain departure at further lowering of temperature. Dulong and Petit law is based on Maxwell-Boltzmaan statistics and Equitation Law. Its departure at lower temperatures implied that quantum mechanics must be used. Einstein found that for quantum harmonic oscillator at energies less than KT, Einstein-Bose statistics must be applied (as in case of black body radiation). The average energy found in statistical distribution of energy in vibrational states is given by

$$E_{average} = \frac{h\upsilon}{\left(e^{\frac{h\upsilon}{KT}} - 1\right)}$$

where υ is frequency of quantum vibrator.

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

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

And specific heat as temperature derivative of energy per mole is

$$C_V = \frac{dE}{dT} = \frac{3N_AK \left(\frac{h\upsilon}{KT}\right)^2 e^{\frac{h\upsilon}{KT}}}{\left(e^{\frac{h\upsilon}{KT}} - 1\right)} \qquad \text{mole}^{-1}$$

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

$$e^{\frac{h\upsilon}{KT}} = 1 + \frac{h\upsilon}{KT}$$

substituting this in above expression of C_V , we get

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

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

Neglecting $\frac{h\upsilon}{KT}$ at high temperatures, Einstein expression reduces to $C_V = 3N_Ak$ 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.

4.1 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 arrieved a maximum allowed phonon frequency called Debye frequency υ_D and defined a Debye temperatute T_D such that

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

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 nonmetals (silicon) but it did not match with experimental results of metals (copper).

4.2 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 cannot. But small number of electrons which are within KT of fermi level contribute a small speific 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

$$C_V = \frac{\pi^2\,N_A\,K^2\,T}{2\,E_f} \qquad \text{mole}^{-1}$$

Debye's Phonon model as discussed above with it's 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.

4.3 Einstein- Debye specific heat

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

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

Electron participation in specific heat suggest that thermal energy is passed 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 be confirmed by understanding behaviour of solids also in which case vibrational degree is of importance. In understanding of absolute temperature, electron specific heat and specific heat curve of solids could also be helpful.

5. Conclusions

Volume of a perfect Gas is not 0 at Absolute Zero Temperature. Since V-T curve of a gas cannot intersect temperature axis at any point, the theoretical limit of -273.15 °C imposed upon temperature as its lower limit is not valid. Yet not experienced, but temperature can assume further any lower value theoretically. Thermal energy is possessed by electrons too at very low temperatures as found and experimentally verified in Einstein - Debye specific heat model. In understanding of absolute temperature, electron specific heat and specific heat curve of solids could also be helpful.

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