

ATOM

Thomson atom model

From the study of discharge of electricity through gases, it became clear that an atom consists of positive and negative charges. J.J. Thomson tried to explain the arrangement of positive charge and the electrons inside the atom.

According to him, an atom is a sphere of positive charge having a radius of the order of 10^{-10}m . The positive charge is uniformly distributed over the entire sphere and the electrons are embedded in the sphere of positive charge .

The total positive charge inside the atom is equal to the total negative charge carried by the electrons, so that every atom is electrically neutral.

According to Thomson, if there is a single electron in the atom (like a hydrogen atom), the electron must be situated at the centre of the positive sphere.

For an atom with two electrons (helium atom), the electrons should be situated symmetrically with respect to the centre of the sphere i.e., opposite sides of the centre at a distance of $r/2$ where r is the radius of the positive sphere. In a three electron system of the atom, the electrons should be at the corners of a symmetrically placed equilateral triangle, the side of which was equal to the radius of the sphere. In general, the electrons of an atom are located in a symmetrical pattern with respect to the centre of the sphere. It was suggested that spectral radiations are due to the simple harmonic motion of these electrons on both sides of their mean positions. Moreover, the stability of the atom was very well explained on the basis of this model

Drawbacks

(i) According to electromagnetic theory, the vibrating electron should radiate energy and the frequency of the emitted spectral line should be the same as the electron. In the case of hydrogen atom,

Thomson's model gives only one spectral line of about 1300 \AA . But the experimental observations reveal that hydrogen spectrum consists of five different series with several lines in each series.

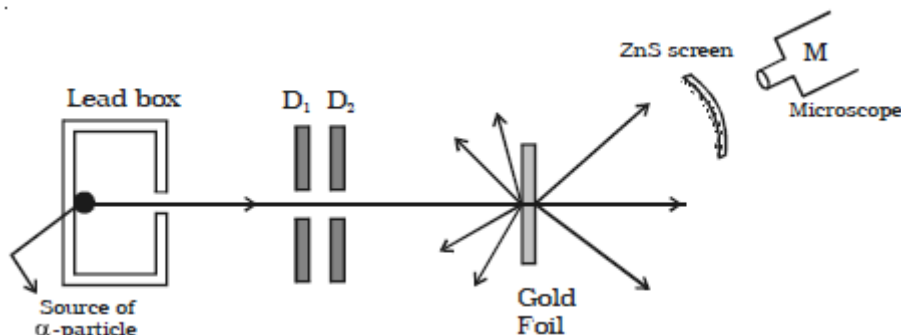
(ii) It could not account for the scattering of α -particles through large angles.

Rutherford's α - particle scattering experiment

Rutherford and his associates studied the scattering of the α - particles by a thin gold foil in order to investigate the structure of the atom. An α -particle is a positively charged particle having a mass equal to that of helium atom and positive charge in magnitude equal to twice the charge of an electron. They are emitted by many radioactive elements. The scattering of α -particles provide useful information about the structure of the atom.

Experimental arrangement

A fine stream of α -particles was obtained from a radioactive material Bi_{83}^{214} by placing it in a lead box with narrow opening as shown in Fig



The α -particles of energy 5.5 MeV emitted from the source in all possible directions, but only a narrow beam emerges from the lead box. The remaining α -particles are absorbed in the lead box itself. After passing through the diaphragms D1 and D2, a narrow beam of α -particles incident on a thin gold foil of thickness 2.1×10^{-7} m, are scattered through different angles.

The scattered α -particles strike a fluorescent screen coated with zinc sulphide. When the α -particles strike the screen, tiny flashes of light are produced.

The observations can be made with the help of a low power microscope.

Observations and conclusions

(i) Most of the α particles either passed straight through the gold foil or were scattered by only small angles of the order of a few degrees.

This observation led to the conclusion that an atom has a lot of empty space.

(ii) A few α particles were scattered in the backward direction, which led Rutherford to conclude that the whole of the positive charge was concentrated in a tiny space of about 10^{-14} m. This region of the atom was named as nucleus. Only a small number of particles approaches the nucleus of the atom and they were deflected at large angles.

Distance of closest approach

An α particle directed towards the centre of the nucleus will move close up to a distance r_0 as shown in Fig, where its kinetic energy will appear as electrostatic potential energy.

After this, the α particle begins to retrace its path. This distance r_0 is known as the distance of the closest approach.

Let m and v be the mass and velocity of the α particle directed towards the centre of the nucleus. Then, the kinetic energy of the particle,

$$E_k = \frac{1}{2}mv^2$$

Since, charge of an α -particle is $2e$ and that of the nucleus of the atom is Ze , the electrostatic potential energy of the α particle, when at a distance r_0 from the centre of the nucleus is given by,

$$E_p = \frac{1}{4\pi\epsilon_0} \frac{(2e)(Ze)}{r_0}$$

where Z is the atomic number of the atom and ϵ_0 , the permittivity of free space.

On reaching the distance of the closest approach r_0 , the kinetic energy of the α particle appears as its potential energy.

$$\begin{aligned} E_p &= E_k \\ \frac{1}{2}mv^2 &= \frac{1}{4\pi\epsilon_0} \frac{(2e)(Ze)}{r_0} \\ r_0 &= \frac{1}{4\pi\epsilon_0} \frac{4Ze^2}{mv^2} \end{aligned}$$

Drawbacks

Rutherford atom model offered serious difficulties as regards the stability of the atom.

Following are the two drawbacks of Rutherford's model:

(i) The electron in the circular orbit experiences a centripetal acceleration. According to electromagnetic theory, an accelerated electric charge must radiate energy in the form of electromagnetic waves.

Therefore, if the accelerated electron loses energy by radiation, the energy of the electron continuously decreases and it must spiral down into the nucleus. Thus, the atom cannot be stable. But, it is well known that most of the atoms are stable.

(ii) According to classical electromagnetic theory, the accelerating electron must radiate energy at a frequency proportional to the angular velocity of the electron. Therefore, as the electron spiral towards the nucleus, the angular velocity tends to become infinity and hence the frequency of the emitted energy will tend to infinity.

This will result in a continuous spectrum with all possible wavelengths. But experiments reveal only line spectra of fixed wavelength from atoms.

Bohr atom model

Neils Bohr in 1913, modified Rutherford's atom model in order to explain the stability of the atom and the emission of sharp spectral lines. He proposed the following postulates:

(i) An electron cannot revolve round the nucleus in all possible orbits. The electrons can revolve round the nucleus only in those allowed or permissible orbits for which the angular momentum of the electron is an integral multiple of $h/2\pi$

(where h is Planck's constant = 6.626×10^{-34} Js).

These orbits are called stationary orbits or non-radiating orbits and an electron revolving in these orbits does not radiate any energy.

If m and v are the mass and velocity of the electron in a permitted orbit of radius r then angular momentum of electron = $mvr = nh/2\pi$,

where n is called principal quantum number and has the integral values 1,2,3 ... This is called Bohr's quantization condition.

(ii) An atom radiates energy, only when an electron jumps from a stationary orbit of higher energy to an orbit of lower energy. If the electron jumps from an orbit of energy E_2 to an orbit of energy E_1 , a photon of energy $h\nu = E_2 - E_1$ is emitted. This condition is called Bohr's frequency condition.

Orbital velocity of electrons

Consider an atom whose nucleus has a positive charge Ze , where Z is the atomic number that gives the number of protons in the nucleus and e , the charge of the electron which is numerically equal to that of proton. Let an electron revolve around the nucleus in the n th orbit of radius r_n .

By Coulomb's law, the electrostatic force of attraction between the nucleus and the electron

$$F_e = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(e)}{r_n^2}$$

Since, the electron revolves in a circular orbit, it experiences a centripetal force

$$\frac{mv_n^2}{r_n}$$

The necessary centripetal force is provided by the electrostatic force of attraction

For equilibrium, from equations

$$\frac{1}{4\pi\epsilon_0} \frac{(Ze)(e)}{r_n^2} = \frac{mv_n^2}{r_n}$$

$$v_n^2 = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(e)}{r_n m}$$

$$v_n = \sqrt{\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n m}} \quad \text{--- eq(1)}$$

Radius of the n^{th} orbit (r_n)

The angular momentum of an electron in n th orbit is,

$$L = mv_n r_n \quad \text{--- eq(2)}$$

By Bohr's first postulate, the angular momentum of the electron

$$L = nh/2\pi \quad \text{--- eq(2)}$$

where n is an integer and is called as the principal quantum number.

From equations. (2) and (2),

$$mv_n r_n = \frac{nh}{2\pi} \quad \text{--- eq(3)}$$

Substituting value of velocity from eq(1)

$$m \sqrt{\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n m}} r_n = \frac{nh}{2\pi}$$

Squaring on both sides

$$m^2 \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n m} r_n^2 = \frac{n^2 h^2}{4\pi^2}$$

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m Z e^2} \text{ --- eq(4)}$$

From equation (4), it is seen that the radius of the nth orbit is proportional to the square of the principal quantum number.

Therefore, the radii of the orbits are in the ratio 1 : 4 : 9....

For hydrogen atom, Z = 1 and n = 1 we get $r_1 = 0.53\text{\AA}$

Energy of an electron in the nth orbit (E_n)

The total energy of the electron is the sum of its potential energy and kinetic energy in its orbit. The potential energy of the electron in the nth orbit is given by,

$$E_p = \frac{1}{4\pi\epsilon_0} \frac{-Ze^2}{r_n}$$

The kinetic energy of the electron in the n^{th} orbit is,

$$E_k = \frac{1}{2} m v_n^2$$

Substituting value of velocity from equation (1)

$$E_k = \frac{1}{2} m \frac{1}{4\pi\epsilon_0} \frac{(Ze)(e)}{r_n m}$$

$$E_k = \frac{1}{8\pi\epsilon_0} \frac{Ze^2}{r_n}$$

Total energy = $E_p + E_k$

$$E = \frac{1}{4\pi\epsilon_0} \frac{-Ze^2}{r_n} + \frac{1}{8\pi\epsilon_0} \frac{Ze^2}{r_n}$$

$$E = \frac{-1}{8\pi\epsilon_0} \frac{Ze^2}{r_n}$$

Substituting value of r_n from equation(4)

$$E = \frac{-Z^2 m e^4}{8\epsilon_0 n^2 h^2} \text{ --- eq(5)}$$

From equation (5), it is seen that the radius of the n^{th} orbit is inversely proportional to the square of the principal quantum number

For hydrogen atom, $Z = 1$, and substituting other values in equation (5) we get

$$E_n = \frac{-13.6}{n^2} \text{ eV} \quad \text{--- eq(6)}$$

As there is a negative sign in equation (6), it is seen that the energy of the electron in its orbit increases as n increases.

Frequency of spectral line

According to Bohr's second postulate, when an electron jumps from an outer orbit of quantum number n to an inner orbit of quantum number m , the frequency of the photon emitted is given by,

$$\nu = \frac{E_m - E_n}{h}$$

Using equation for energy, equation(6)

$$\nu = \frac{Z^2 m e^4}{8 \epsilon_0^2 h^3} \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \quad \text{--- eq(7)}$$

The wave number $\bar{\nu}$ of a radiation is defined as number of waves per unit length. It is equal to reciprocal of the wavelength

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad [\because c = \nu \lambda]$$

From equation(7)

$$\bar{\nu} = \frac{Z^2 m e^4}{8 \epsilon_0^2 c h^3} \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \quad \text{--- eq(8)}$$

For Hydrogen $Z = 1$

$$\bar{\nu} = \frac{m e^4}{8 \epsilon_0^2 c h^3} \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

$$\bar{\nu} = R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

where R is a constant called Rydberg's constant

Substituting the known values, we get $R = 1.094 \times 10^7 \text{ m}^{-1}$

Spectral series of hydrogen atom

Whenever an electron in a hydrogen atom jumps from higher energy level to the lower energy level, the difference in energies of the two levels is emitted as a radiation of particular wavelength.

It is called a spectral line. As the wavelength of the spectral line depends upon the two orbits (energy levels) between which the transition of electron takes place, various spectral lines are obtained.

The different wavelengths constitute spectral series which are the characteristic of the atoms emitting them. The following are the spectral series of hydrogen atom.

(i) Lyman series

When the electron jumps from any of the outer orbits to the first orbit, the spectral lines emitted are in the ultraviolet region of the spectrum and they are said to form a series called Lyman series

$$\bar{\nu} = R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

Here $n = 1$ and $m = 2, 3, 4, \dots$

$$\bar{\nu} = R \left(1 - \frac{1}{m^2} \right)$$

(ii) Balmer series

When the electron jumps from any of the outer orbits to the second orbit, we get a spectral series called the Balmer series. All the lines of this series in hydrogen have their wavelength in the visible region. Here $n=2$, $m = 3, 4, 5 \dots$. The wave number of the Balmer series is,

$$\bar{\nu} = R \left(\frac{1}{2^2} - \frac{1}{m^2} \right)$$

The first line in this series ($m = 3$), is called the H_{α} -line, the second ($m=4$), the H_{β} -line and so on.

(iii) Paschen series

This series consists of all wavelengths which are emitted when the electron jumps from outer most orbits to the third orbit. Here $m = 4, 5, 6 \dots$ and $n = 3$. This series is in the infrared region with the wave number given by

$$\bar{\nu} = R \left(\frac{1}{3^2} - \frac{1}{m^2} \right)$$

(iv) Brackett series

The series obtained by the transition of the electron from $m = 5, 6 \dots$ and $n = 4$ is called Brackett series. The wavelengths of these lines are in the infrared region. The wave number is

$$\bar{\nu} = R \left(\frac{1}{4^2} - \frac{1}{m^2} \right)$$

(v) Pfund series

The lines of the series are obtained when the electron jumps from any state $m = 6, 7 \dots$ and $n=5$. This series also lies in the infrared region. The wave number is,

$$\bar{\nu} = R \left(\frac{1}{5^2} - \frac{1}{m^2} \right)$$

Shortcomings of Bohr's theory

Bohr's theory was able to explain successfully a number of experimental observations and has correctly predicted the spectral lines of hydrogen atom. However, the theory fails in the following aspects.

- (i) The theory could not account for the spectra of atoms more complex than hydrogen.
- (ii) The theory does not give any information regarding the distribution and arrangement of electrons in an atom.
- (iii) It does not explain the experimentally observed variations in intensity of the spectral lines of the element.
- (iv) When the spectral line of hydrogen atom is examined by spectrometers having high resolving power, it is found that a single line is composed of two or more close components. This is known as the fine structure of spectral lines. Bohr's theory could not account for the fine structure of spectral lines.
- (v) It is found that when electric or magnetic field is applied to the atom, each of the spectral line split into several lines. The former effect is called as Stark effect, while the latter is known as Zeeman effect.

Excitation and Ionization Potential

Suppose electron revolving in a stationary orbit of an atom absorbs specific energy, and jumps to an orbit of higher energy. This process is called excitation and the atom is said to be in the excited state. The energy absorbed to move electron from one orbit to the other is called excitation potential,

If $n = 1$ is called ground state, $n = 2$ is called first excited state, $n = 3$ is called second excited state

If the energy supplied is large enough to remove an electron from the atom, then the atom is said to be ionized. The minimum energy needed to ionize an atom is called ionization energy. Note that energy for $n = \infty$ is taken as zero.

The minimum amount of energy to release an electron from ground state is called the first or principal ionization energy. The ionization of electrons from higher energy state is termed depending on their quantum number. For $n = 2$, second ionization energy, for $n = 3$, third ionization energy etc.

De Broglie's explanation of Bohr's second postulate of quantization

Since the electron does not radiate energy in stationary orbits, the De Broglie wave associated with it must be a stationary wave. The electron-wave selects only those orbits for which the circumference of the orbit is equal to an integral number (n) of the associated de Broglie wavelength. If it is not then, each wave traveling around the orbit will not be in phase and would interfere in such a way that their average intensity would be zero. In this case, an electron cannot be found in such an orbit.

Thus, necessary condition for permitted orbits is

$$2\pi r = n\lambda$$

Where n = number of waves (integer) and r = radius of orbit

And λ = wavelength of de Broglie wave = h/mv

$$\therefore 2\pi r = \frac{nh}{mv}$$

Now angular momentum

$$l = mvr = \frac{nh}{2\pi}$$

Solved Numerical

Q) The wavelength of the K_α line emitted by a hydrogen atom like element is 0.32\AA . Determine the wavelength of K_β line emitted by the same element

Solution

From formula for hydrogen like element

$$\bar{\nu} = \frac{1}{\lambda} = R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

For K_α $n = 1$ and $m = 2$

$$\frac{1}{0.32 \times 10^{-10}} = R \left(1 - \frac{1}{2^2} \right)$$

$$\frac{1}{0.32 \times 10^{-10}} = R \left(\frac{3}{4} \right) \quad \text{--- eq(1)}$$

For K_β $n = 1$ and $m = 3$

$$\frac{1}{\lambda} = R \left(1 - \frac{1}{3^2} \right)$$

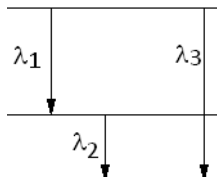
$$\frac{1}{\lambda} = R \left(\frac{8}{9} \right) \quad \text{--- eq(2)}$$

Taking ratio of equation (1) and (2) we get

$$\lambda = 0.32 \times 10^{-10} \left(\frac{3}{4} \right) \left(\frac{9}{8} \right) = 0.27 \times 10^{-10}$$

$$\lambda = 0.27 \text{\AA}$$

Q) Find the relation between three wavelengths $\lambda_1, \lambda_2, \lambda_3$ from the energy level diagram shown in figure



Solution

From figure $E_3 = E_1 + E_2$ thus

$$\frac{hc}{\lambda_3} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$

$$\frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\lambda_3 = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$$

Q) The wavelength of first line of Lyman series of hydrogen is identical to that of the second line of Balmer series for some hydrogen like ion X. Calculate energies of the first four levels of X. Also find its ionization potential (Given: Ground state binding energy of hydrogen atom 13.6 eV)

Solution:

From the formula

$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

For first line of Lyman series of hydrogen $Z = 1$, $n = 1$ and $m = 2$

$$\frac{1}{\lambda} = R \left(1 - \frac{1}{2^2} \right) = R \left(\frac{3}{4} \right) \quad \text{--- eq(1)}$$

For second line of Balmer series of X, $n = 2$ and $m = 4$

$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

$$\frac{1}{\lambda} = ZR \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = Z^2 R \left(\frac{3}{16} \right) \quad \text{--- eq(2)}$$

From equation (1) and (2)

$$R \left(\frac{3}{4} \right) = Z^2 R \left(\frac{5}{16} \right)$$

$$Z = 2$$

From the formula for energy of electron in nth orbit

$$E = \frac{-Z^2 m e^4}{8 \epsilon_0 n^2 h^2}$$

For ionization potential $n = 1$

Ionization potential for H ; $Z = 1$

$$E_H = \frac{-m e^4}{8 \epsilon_0 h^2}$$

Ionization potential for X ; $Z = 2$

$$E_X = \frac{-2^2 m e^4}{8 \epsilon_0 h^2} = 4 E_H$$

$$E_x = 4 \times (-13.6) = 54.4 \text{ eV}$$

Ionization potential of x = 54.4 eV

Energy of ground state or first energy level n=1

$$E_2 = \frac{-54.4}{1^2} = -54.4 \text{ eV}$$

Energy of first excited state or second energy level n = 2

$$E_2 = \frac{-54.4}{2^2} = -13.6 \text{ eV}$$

Energy of first excited state or third energy level n = 3

$$E_3 = \frac{-54.4}{3^2} = -6.04 \text{ eV}$$

Energy of first excited state n = 4 or fourth energy level n = 4

$$E_3 = \frac{-54.4}{4^2} = -3.4 \text{ eV}$$

Q) A body of mass m is attached at one end of spring of force constant K. It is given a motion on a circular path of radius r. Assuming that there are integer number of waves representing this particle on the circumference of the circle and using Bohr's quantum condition prove that the quantized energy is given by $E_n = nh\omega/2\pi$

given angular frequency $\omega = \sqrt{\frac{k}{m}}$

Solution:

Total energy = Kinetic energy + spring potential energy

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kr^2 \text{ --- eq(1)}$$

Here k is restoring force constant of spring and $k = m\omega^2$ and $\omega = v/r$

$$k = \frac{mv^2}{r^2}$$

On substituting value of k in equation (1) we get

$$E = \frac{1}{2}mv^2 + \frac{1}{2}mv^2 = mv^2 \text{ --- eq(2)}$$

According to Bohr's postulate angular momentum

$$mvr = \frac{nh}{2\pi}$$

$$\therefore mv^2 = \frac{nhv}{2\pi r} \text{ --- eq(3)}$$

From equation(2) and (3) we get

$$E = \frac{nhv}{2\pi r}$$

But $\omega = v/r$

$$\therefore E = \frac{nh\omega}{2\pi}$$

Q) Suppose the potential energy between electron and proton at a distance r is given by $-ke^2/3r^3$. Use Bohr's theory to obtain energy levels of such a hypothetical atom

Solution:

We know that for conservative force field

$$F = -dU/dr$$

$$\therefore F = -\frac{d}{dr}\left(\frac{ke^2}{3r^3}\right) = \frac{ke^2(3)}{3r^4} = \frac{ke^2}{r^4}$$

Now electrostatic force = centripetal force at equilibrium

$$\frac{ke^2}{r^4} = \frac{mv^2}{r}$$

$$\therefore v^2 = \frac{ke^2}{r^3}$$

Now according to Bohr's postulate

$$mvr = \frac{nh}{2\pi}$$

Squaring on both sides

$$m^2v^2r^2 = \frac{n^2h^2}{(2\pi)^2}$$

Substituting value of v

$$m^2 \frac{ke^2}{r^3} r^2 = \frac{n^2h^2}{(2\pi)^2}$$

$$r = \frac{m^2ke^2(2\pi)^2}{n^2h^2}$$

Now we know that total energy of electron = (1/2) potential energy

$$\therefore E = \frac{ke^2}{6r^3}$$

By substituting value of r from above

$$E = \frac{ke^2}{6} \frac{(n^2h^2)^3}{(m^2ke^2(2\pi)^2)^3}$$

$$\therefore E = \frac{(nh)^6}{6(ke^2)^2m^3(2\pi)^6}$$

Q) The energy of an electron in an excited hydrogen atom is -3.4eV. Determine the angular momentum using Bohr's theory. Given: Ground state energy of hydrogen atom = -13.6 eV

Solution:

$$-3.4 = -\frac{13.6}{n^2}$$

n=2

Angular momentum

$$L = \frac{nh}{2\pi} = \frac{2 \times 6.625 \times 10^{-34}}{2 \times 3.14} = 2.1 \times 10^{-34} Js$$

Q) At what temperature will the average molecular kinetic energy in gaseous hydrogen be equal to the binding energy of a hydrogen atom? Boltzmann constant $k_B = 1.3 \times 10^{-23} \text{ JK}^{-1}$

Solution

Kinetic energy of molecule of gas is given by $\frac{3}{2} k_B T$

$$\therefore \frac{3}{2} k_B T = 13.6 eV$$

$$T = \frac{13.6 \times 1.6 \times 10^{-19} \times 2}{3 \times k_B}$$

$$T = \frac{13.6 \times 1.6 \times 10^{-19} \times 2}{3 \times 1.3 \times 10^{-23}} = 11.16 \times 10^4$$

$$T = 1.116 \times 10^5 K$$

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