

The Ring cum Vacancy Mechanism of Diffusion in Pure Metals

Gaurav Kumar

Department of Metallurgical and Materials Engineering, National Institute of Technology, Durgapur, India

Abstract: *The experimentally determined self diffusion coefficient of copper has been found to deviate from that predicted by vacancy mechanism at lower temperatures (below 900 Celsius). Such behaviour is not unexpected since vacancy concentration in metals rapidly decreases with decreasing temperature following an exponential relationship. This means that the vacancy mechanism cannot be the principal driving mechanism for self diffusion copper and there must be an alternative mechanism occurring at those temperatures. This paper explores the possibility of that alternative mechanism with the help of the mathematical model validated against the experimental diffusivity data at the experimental temperatures. With this validation it is found that a mixed diffusion mechanism which is a conjoint of two different mechanisms (vacancy and ring diffusion mechanism) can be that alternative mechanism driving the self-diffusion in copper at lower temperatures*

Keywords: Diffusion, Mixed mechanism, Ring Mechanism, Vacancy Mechanism, Vacancies, Activation Energy, Jump Frequency, Atomistic Model, Theoretical

1. Introduction

Understanding and exploitation of phase transformation at solid state stems the development of new material containing desired phases to meet the properties necessary for real life applications. Diffusion is a process of fundamental significance for many phase transformations at solid state. Confining to purely chemical system, diffusion is the process by which an atom migrates from a region of higher chemical potential to a region of lower chemical potential. The mechanism for this migration becomes a subject of endeavour. Altogether there are five kinds of solid state diffusion mechanism proposed so far, namely, Vacancy mechanism, interstitial mechanism, Interstitialcy mechanism, direct interchange mechanism and Ring mechanism [1]. In case of self diffusion of metals, till date, the vacancy mechanism is believed to be the principal mechanism. In an early study by Huntington & Seitz [2], it was shown that an interchange of two neighbouring atoms (direct interchange mechanism) would require much more activation energy than the observed heat of activation. Through an exhaustive analytical treatment on the basis of interatomic force and associated energy calculations, much higher activation energy requirement was revealed for direct interchange mechanism in comparison with vacancy mechanism. Furthermore, the heat of activation was found to be consistent with the concept of self-diffusion occurring by the process of vacancy mechanism. Zener [1] put forward the theory of ring mechanism; where diffusion was theoretically conceived to occur through rotation of a group of atoms (preferably 4 atoms) in the form of a ring. In such a philosophy, direct interchange mechanism becomes a part of ring mechanism involving rotation of a two-atom ring. In his work Zener [1] explored much lower activation energy for rotation of a four-atom ring than that for rotation of a two-atom ring (direct interchange mechanism). In that formulation the energy of the lattice was considered to be the summation of three energy terms; namely, (1) energy pertaining to coulomb interaction, (2) energy for repulsive exchange interaction, and (3) the energy term accounting for all other types of energy. However, the apparent complicity

of the analytical treatment could not allow a direct comparison of activation energies between 4-ring diffusion mechanism and vacancy mechanism. This complicity of 'interatomic force and associated energy'-based calculations was resolved later on with analytical calculations for diffusion coefficient on the basis of the concept of 'jump-frequency'. Accordingly, the analytical expressions of diffusion coefficient for vacancy mechanism and interstitial mechanism are readily available [8]. However, the analytical calculation of diffusion coefficient for ring mechanism is still awaited. Furthermore, the experimentally determined self diffusion coefficient of copper has been found to deviate from that predicted by vacancy mechanism at lower temperatures (below 900°C) [4]. Such behaviour is not unexpected since vacancy concentration in metals rapidly decreases with decreasing temperature following an exponential relationship [8]. Moreover, the region of lattice devoid of vacancy is likely to follow a different mechanism (preferably ring mechanism); whilst the region containing vacancies would follow vacancy mechanism. This argument asks for introspection in a conjoint occurrence of vacancy mechanism and ring mechanism for self diffusion. The Present study aims to revisit the diffusion mechanisms and explore the possibility of this conjoint occurrence of vacancy and ring mechanism by (1) an analytical calculation of diffusion coefficient for ring mechanism and (2) proposition of a 'Mixed Mechanism', a combination of 'Vacancy Mechanism' and 'Ring Mechanism' along with analytical calculation of diffusion coefficient. The analytical model of the mixed mechanism is validated against the existing experimental data for self diffusion of copper at lower temperatures.

The first step would be to revisit the vacancy mechanism and the derivation of its diffusivity expression with the help of the atomistic model of jump frequency [8].

If the number of successful jumps by an atom per second is denoted as τ

Then according to the atomistic approach τ =(number of successful jumps executed by an atom having the right energy to overcome the activation energy barrier)*(probability of an atom executing jump in all direction).

$$\text{And } \tau = z\nu e^{\frac{-(\Delta G_m + \Delta G_f)}{RT}} \quad [8] \quad (1)$$

Where,

ΔG_m : Free energy for migration of 1 mol of atoms from normal state to activated state.

ΔG_f : The free energy for formation of 1 mol of vacancies

T: Absolute temperature

R: Universal gas constant.

Z: Co-ordination number of lattice

ν : Jump Frequency

Atomistic approach of diffusivity relates the diffusivity D to

the jump frequency τ as $D = \frac{1}{6} \tau \alpha^2$ (for random jumps) [8].

$$\text{So } D = \frac{1}{6} z\nu e^{\frac{-(\Delta G_m + \Delta G_f)}{RT}} \alpha^2 \quad (2)$$

Where α : the centre to centre distance between atoms

So now comparing the diffusivities for BCC and FCC metals

For FCC metals $\alpha = \frac{a}{\sqrt{2}}$ and $z = 12$ and for BCC

metals $\alpha = \frac{a\sqrt{3}}{2}$ and $z = 8$ where a is the lattice parameter of metals [9].

$$\text{So } D_{FCC} = a^2 \nu e^{\frac{-(\Delta G_m + \Delta G_f)}{RT}}$$

$$\text{And } D_{BCC} = a^2 \nu e^{\frac{-(\Delta G_m + \Delta G_f)}{RT}}$$

Now;

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\Delta G_f = \Delta H_f - T\Delta S_f$$

$$\text{So } D_{BCC} = a^2 \nu e^{\frac{(\Delta S_m + \Delta S_f)}{R}} e^{\frac{-(\Delta H_m + \Delta H_f)}{RT}} = D_0 e^{\frac{-(\Delta H_m + \Delta H_f)}{RT}} \quad (3)$$

$$\text{And } D_{FCC} = a^2 \nu e^{\frac{(\Delta S_m + \Delta S_f)}{R}} e^{\frac{-(\Delta H_m + \Delta H_f)}{RT}} = D_0 e^{\frac{-(\Delta H_m + \Delta H_f)}{RT}} \quad (4)$$

$$\text{Where } D_0 = a^2 \nu e^{\frac{(\Delta S_m + \Delta S_f)}{R}}$$

(ΔH_m denotes enthalpy change during migration of 1 mol of atom from normal state to activated state, ΔS_m denotes entropy change during migration of 1 mol of atom from normal state to activated state, ΔH_f denotes the enthalpy change for formation of 1 mol of vacancies and ΔS_f denotes the entropy change for formation of 1 mol vacancies)

(Note: the vacancy mechanism stated above is considered assuming the fact it is the only principal mechanism driving the self-diffusion in pure metals and so later in this paper the vacancy mechanism and pure vacancy mechanism will mean the same).

Now the vacancy (the vacant lattice sites) concentration is function of absolute temperature and the relationship can be determined quantitatively [8]

If the activation energy for creating 1 mol of vacancy is denoted as ΔH_f

$$\text{So } \frac{n_{vac}}{N} = e^{\frac{-\Delta H_f}{RT}} \quad (5)$$

Where

n_{vac} : Number of vacant lattice sites

N: Total number of lattice sites

$\frac{n_{vac}}{N}$: Vacancy concentration

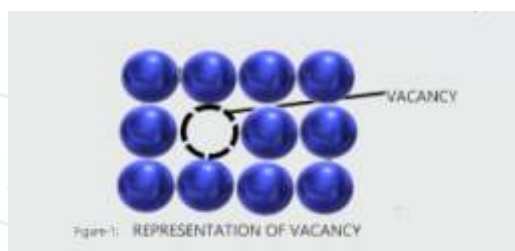


Figure 1

From the above expression it is clear that with decrease in temperature the vacancy concentration will also decrease, so at lower temperature due to the scarcity of vacancies (in comparison to the higher temperatures) a pure vacancy mechanism may not be the only driving mechanism of diffusion, so at lower temperature ranges exploring some other mechanism where the involvement of vacancies is much lesser than the pure vacancy mechanism becomes important.

2. The Ring Mechanism

The ring diffusion mechanism involves the rotation of a number of atoms in the form of a ring in clockwise or anticlockwise fashion. An atom can take more than one ring and can migrate from one location to other. But if a closer observation is made in for the ring mechanism then it can be seen that basically the ring mechanism is a “sequential, systematic and co-operative vacancy mechanism” where the atoms jumps into the vacancy (spontaneously created) of the adjacent member atom of the ring.

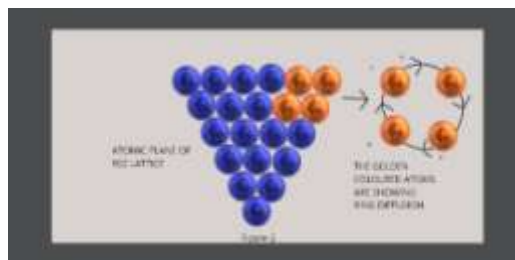


Figure 2

Figure 2 depicts the process of ring mechanism(here in FCC lattice) the golden coloured atoms are considered for ring rotation here as can be seen after rotation atom 1 takes position of atom 2 ,atom 2 takes position of atom 3 and atom

3 takes position of atom 4 by a “sequential, systematic and co-operative vacancy mechanism”.

2.1 The Mathematical Model

2.1.1 Assumptions

1. The number of atoms in a ring i.e. the size of the ring will be same all over the lattice

2. The ring will be completely free to rotate clockwise and anti-clockwise.

Now for the transformation Atom at normal state -----> Atom at activated state

ΔG_m : Free energy for migration of 1 mol of atoms from its normal state to activated state.

n^* : Number of atoms at activated state.

n : Number of atoms at normal state

N : Total number of atoms.

$$N = n^* + n$$

And

$$\Delta G_m = -RT \ln K_1 \quad (6)$$

Where K_1 is the equilibrium constant for above transformation

$$K_1 = \frac{\text{activity of product}}{\text{activity of reactant}} = \frac{\frac{n^*}{n+n^*}}{\frac{n}{n+n^*}} = \frac{n^*}{n} \quad (7)$$

Since $N = n^* + n$ and $N \gg n^*$ but since $N \approx n$

$$\text{Therefore } K_1 = \frac{n^*}{N} \quad (8)$$

So $\Delta G_m = -RT \ln \frac{n^*}{N}$ so $\frac{n^*}{N} = e^{\frac{-\Delta G_m}{RT}}$ and $\frac{n^*}{N}$ is the probability that an atom will be at its activated state.

If ν is the jump frequency of the atom then number of jumps per second executed by an atom having the right energy to overcome the activation energy barrier is

$$\nu \frac{n^*}{N} = \nu e^{\frac{-\Delta G_m}{RT}} \quad (9)$$

The second step is to determine the probability that the adjacent site of the activated atom will be vacant.

If n_v number of vacant sites

n_1 : Number of normal sites.

N_1 : Total number of lattice sites.

Now an atom in a ring will find its adjacent site vacant if its adjacent member atom of ring will migrate to new position in the ring. So free energy for finding an adjacent site vacant will also be ΔG_m . (This is in contrast to the value ΔG_f used in the derivation of diffusivity expression for pure vacancy mechanism).

So, ΔG_m : the free energy for formation of 1 mol of vacancies

For the transformation

Atom at normal lattice site \rightarrow Atom at vacant lattice site

$$\Delta G_m = -RT \ln K_2 \quad (10)$$

Where K_2 is the equilibrium constant for above transformation

$$K_2 = \frac{\text{activity of product}}{\text{activity of reactant}} = \frac{\frac{n_v}{n+n_v}}{\frac{n}{n+n_v}} = \frac{n_v}{n}$$

Since $N_1 = n_1 + n_v$ and $N_1 \gg n_v$, as number of vacancies (or vacant sites) would be very less in comparison

to total number of lattice sites so $K_2 = \frac{n_v}{N}$

Therefore $\Delta G_m = -RT \ln \frac{n_v}{N_1}$, and $\frac{n_v}{N_1} = e^{\frac{-\Delta G_m}{RT}}$ is the probability that the lattice site is vacant.

Now a ring of atoms can either rotate clockwise or anti-clockwise, if ring rotates in clockwise direction then all member atoms will be bound to rotate in the clockwise direction (for example in a clockwise rotating ring if any member atom takes opposite direction (anti-clockwise direction) to migrate then the whole ring will be distorted) so all member atoms of the ring will have only one possible direction to migrate at a time which will be either clockwise (for clockwise rotating ring) or anti-clockwise (for anti-clockwise rotating ring). So the probability that an atom will execute jump in all directions is

$$1 \cdot \frac{n_v}{N} = 1 \cdot e^{\frac{-\Delta G_m}{RT}} = e^{\frac{-\Delta G_m}{RT}} \quad (11)$$

If the number of successful jumps by an atom in a ring per second is denoted by τ_r

Then τ_r = (number of successful jumps executed by an atom having the right energy to overcome the activation energy barrier) * (probability of an atom executing jump in all direction in the ring)

Therefore

$$\tau_r = \left(\nu \frac{n^*}{N}\right) \left(1 \cdot \frac{n_v}{N}\right) = \left(\nu e^{\frac{-\Delta G_m}{RT}}\right) \left(1 \cdot e^{\frac{-\Delta G_m}{RT}}\right) = \nu e^{\frac{-2\Delta G_m}{RT}} \quad (12)$$

By atomistic approach of diffusion [8] $D = \frac{1}{6} \tau \alpha^2$

$$\text{So } D_r = \frac{1}{6} \nu e^{\frac{-2\Delta G_m}{RT}} \alpha^2 = \frac{1}{6} \nu e^{\frac{2\Delta S_m}{R}} \cdot e^{\frac{-2\Delta H_m}{RT}} \alpha^2 = D_o e^{\frac{-2\Delta H_m}{RT}} \quad (13)$$

where $D_o = \frac{1}{6} \nu e^{\frac{2\Delta S_m}{R}} \alpha^2$ and α is the distance between adjacent atoms. In FCC metals

$\alpha = \frac{a}{\sqrt{2}}$ where a is the lattice parameter of metal [9].

(ΔH_m denotes enthalpy change during migration of 1 mol of atom from normal state to activated state, ΔS_m denotes entropy change during migration of 1 mol of atom from normal state to activated state). The ring mechanism of

diffusion does not take into account the already present vacancies at the given temperatures so this mechanism can be the most likely mechanism of diffusion at places devoid of vacancies (the number of vacant sites here taken as n_v are those which are formed when the member atoms of the rotating ring jumps to the adjacent vacant site so created by the adjacent member atom of ring during ring rotation so as a whole there is no use of already present vacant lattice sites during ring diffusion).

3. The Ring cum Vacancy Mechanism

It is right to say that the vacancy concentration will decrease with decrease in temperature but at the same time it must be kept in mind that no matter how pure is the element sample, it cannot be completely devoid of vacancies since vacancy is a stable defect so even at low temperatures there will be some vacancy concentration and here along with ring mechanism yet another diffusion mechanism which is neither pure vacancy nor pure ring but a combination or conjoint of both should be considered.

3.1 Modelling

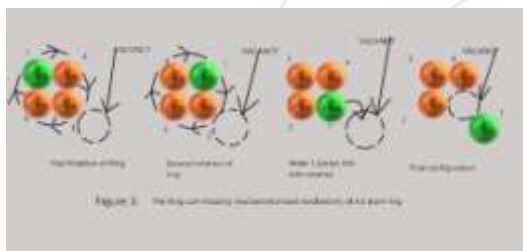


Figure 3

As in figure 3 the atom 1 first rotates (according to the ring mechanism) then jumps to the vacancy (shown) by dotted lines.

We will now proceed by definitions; the jump frequency is the number of successful jumps per second executed by an atom

So if τ is the jump frequency then 1 successful jump will be executed in $\frac{1}{\tau}$ seconds.

Let $\tau_{\mathfrak{R}}$ be the number of successful jumps per second executed by an atom in ring diffusion mechanism (during ring rotation) and τ_v be the number of successful jumps per second executed by an atom in vacancy mechanism (jump into vacancy). For first rotation of a ring (as in figure 3) each atom in the ring will execute 1 jump and therefore will take $\frac{1}{\tau_{\mathfrak{R}}}$ seconds. After reaching near the vacancy the atom will make 1 jump into the vacancy (as seen for atom 1 in figure 3) the time taken by such jump will be $\frac{1}{\tau_v}$ seconds.

So we will find the number of successful jumps per second executed by an atom for this mechanism denoted as τ_{mix} .

$$\text{Now } \tau_{mix} = \frac{\text{total number of successful jumps}}{\text{total time elapsed for those successful jumps}} \quad (14)$$

Now let n_r be the number of ring jumps (jumps during the ring rotation) and n_v the number of vacancy jumps (jumps into the vacancy) i.e. a total of $n_r + n_v$ jumps for the mixed (ring cum vacancy mechanism).

So total time elapsed is $\frac{n_r}{\tau_{\mathfrak{R}}}$ seconds for the ring rotation

and $\frac{n_v}{\tau_v}$ seconds for the jump into vacancy.

$$\text{So } \tau_{mix} = \frac{n_r + n_v}{\frac{n_r}{\tau_{\mathfrak{R}}} + \frac{n_v}{\tau_v}} \quad (15)$$

Now the question is how many jumps an atom will make i.e. how many times the ring will rotate before jumping into the vacancy? Now at this two points must be considered

- 1) More diffusion distance (i.e. more successful jumps per second) means more rotation of ring which enhances diffusivity.
- 2) More rotation of ring (i.e. more successful sequential and systematic jump per second) distorts and disturbs the neighbouring atoms and can increase the energy of the system which is not desirable.

The above points are conflicting with each other.

In a ring an atom can make either no jump (i.e. no rotation of ring and simply the nearest atom will jump into the vacancy) or at most the atom in a ring of \mathfrak{R} atoms will make \mathfrak{R} jumps and come to its initial position and then jump into vacancy (full round ring rotation).

We need to negotiate between the two above points and after negotiation one may come to a conclusion that in a ring of \mathfrak{R} atoms, an atom will jump $\frac{\mathfrak{R}}{2}$ times in the ring and then jump into the vacancy (this means that the size and position of the ring will be such that an atom after executing $\frac{\mathfrak{R}}{2}$ jumps (in a ring of \mathfrak{R} atoms) will get a vacant site adjacent to it).

Zener[1] in his work concluded that a 4 atom ring will be energetically favourable, so going on the lines of Zener here also a 4 atom ring is considered and so in the mixed mechanism the atom will execute 2 ring jumps and one vacancy jump to finally jump into the vacancy. So $n_r = 2; n_v = 1; n_r + n_v = 3$ so

$$\tau_{mix} = \frac{3}{\frac{2}{\tau_{\mathfrak{R}}} + \frac{1}{\tau_v}} \quad (16)$$

By atomistic approach of diffusion [8].

$$D_{mix} = \frac{1}{6} \tau_{mix} \alpha^2 \quad (17)$$

Where α is the centre to centre distance between adjacent atoms. In FCC metals $\alpha = \frac{a}{\sqrt{2}}$ where a is the lattice parameter of metal [9].

$$D_{vac(FCC)} = \frac{1}{6} \tau_v \alpha^2 = a^2 \nu e^{\frac{(\Delta S_m + \Delta S_f)}{RT}} e^{\frac{-(\Delta H_m + \Delta H_f)}{RT}}$$

$$D_{ring} = \frac{1}{6} \tau_{\text{ring}} \alpha^2 = \frac{1}{6} \nu e^{\frac{-2\Delta G_m}{RT}} \alpha^2 = \frac{1}{6} \nu e^{\frac{2\Delta S_m}{R}} \cdot e^{\frac{-2\Delta H_m}{RT}} \alpha^2 = D_o e^{\frac{-2\Delta H_m}{RT}}$$

Where $D_o = \frac{1}{6} \nu e^{\frac{2\Delta S_m}{R}} \alpha^2$ and $\alpha = \frac{a}{\sqrt{2}}$ for FCC lattice [9]

And $D_{mix} = \frac{1}{6} \tau_{mix} \alpha^2$ where $\tau_{mix} = \frac{n_r + n_v}{\frac{n_r}{\tau_{\text{ring}}} + \frac{n_v}{\tau_v}}$ with $n_r = 2; n_v = 1; n_r + n_v = 3$ so $\tau_{mix} = \frac{3}{\frac{2}{\tau_{\text{ring}}} + \frac{1}{\tau_v}}$. For

calculation of diffusivities, data of appropriate variables: 'a' (lattice parameter of copper)[7], ΔS_m (entropy of migration of atom of copper)[5], ΔS_f (entropy of formation of vacancy in copper)[5], ΔH_m (enthalpy of migration of atom of copper)[5], ΔH_f (enthalpy of formation of vacancy in copper)[5], Jump frequency $\nu = \frac{1}{a} \sqrt{\frac{\Delta H_m}{M}}$ (where M is the average atomic mass of atoms making up the lattice and ΔH_m is the enthalpy of migration of atom) [5] are taken. (These values (given in literature) are appropriately converted into Standard International (SI) units).

3. Two plots of diffusivity (m²/sec) vs. temperature (Kelvin) are made. The first plot contains all 8 data points of experimental data taken from Kuper [4] and theoretical data of vacancy, ring and mixed diffusion mechanism. The second plots contain the lower temperature 6 data points for clarity purpose (as these data points have become eclipsed in PLOT 1).

4. 4 plots of lnD vs. 1000/T (Arrhenius plots) are made. The first plot is of the experimental data taken from Kuper[4]. The rest 3 are lnD vs. 1/T plots (Arrhenius plots) of theoretical diffusivity data for vacancy mechanism, ring mechanism, mixed (ring cum vacancy) mechanism (here D stands for diffusivity (m²/sec) and T stands for absolute temperature (Kelvin)).

5. Result and Discussion

1. The following table (TABLE 1) gives the diffusivity values (in m²/sec) at the 8 experimental temperatures taken by Kuper [4]

4. Steps for Validation of Mathematical Model

- 1) The experimental self diffusivity values (m²/sec) at their respective experimental temperatures are taken from Kuper et al [4].
- 2) The theoretical diffusivity values (m²/sec) are calculated according to their respective mathematical expressions:

Table 1

(exp) (K)	Dexp (m ² /sec)	Dvac(theo) (m ² /sec)	Dring(theo) (m ² /sec)	Dmix(theo) (m ² /sec)
1336.15	4.12E-13	2.48982E-13	5.54917E-13	3.93675E-13
1209.85	5.91E-14	3.84603E-14	1.37351E-13	7.39608E-14
1112.15	1.05E-14	6.77891E-15	3.75209E-14	1.49388E-14
1085.35	6.8E-15	3.98704E-15	2.5232E-14	9.08878E-15
1038.35	2.2E-15	1.47118E-15	1.19747E-14	3.54299E-15
988.65	7.92E-16	4.62409E-16	5.04088E-15	1.17218E-15
957.95	3.71E-16	2.13051E-16	2.8242E-15	5.55363E-16
933.35	2.53E-16	1.10366E-16	1.72723E-15	2.93579E-16

The above table shows the experimental diffusivity data as well as theoretically determined diffusivity data (vacancy, ring and mixed mechanism) at the experimental temperatures. (The temperatures in Celsius are converted to Kelvin as $T^{oC} = T^K + 273.15$ [6]).

2. The following table shows the % deviation of experimental diffusivity data from that of the theoretical

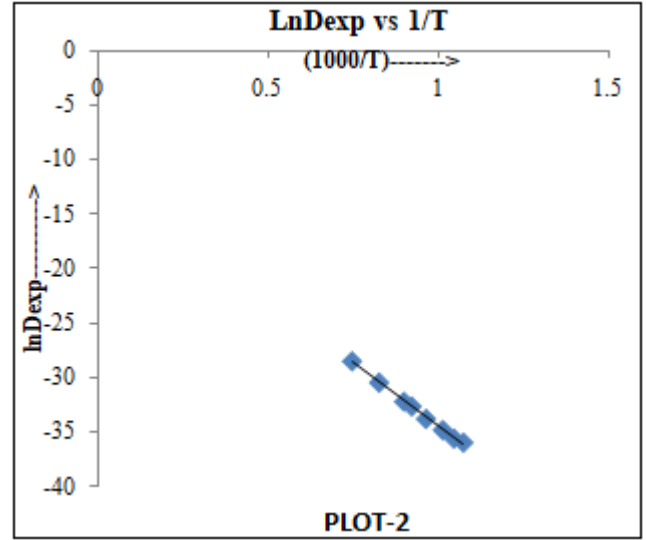
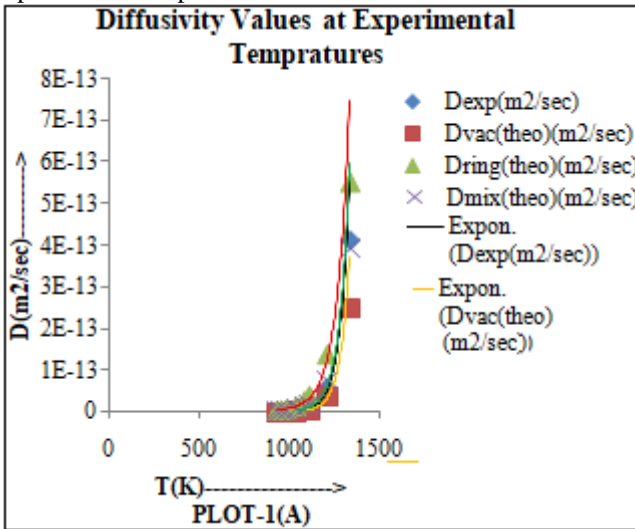
one, so % deviation = $\left| \frac{D_{\text{experimental}} - D_{\text{theoretical}}}{D_{\text{theoretical}}} \right| \times 100$. Here

there will be 3 % deviations: 1. deviation of experimental data from that of theoretical data of vacancy mechanism ($\Delta D/D\%$ (vac)), 2. deviation of experimental data from that of theoretical data of ring mechanism ($\Delta D/D\%$ (ring)), 3. deviation of experimental data from that of theoretical data of mixed (ring cum vacancy) mechanism ($\Delta D/D\%$ (mix)).

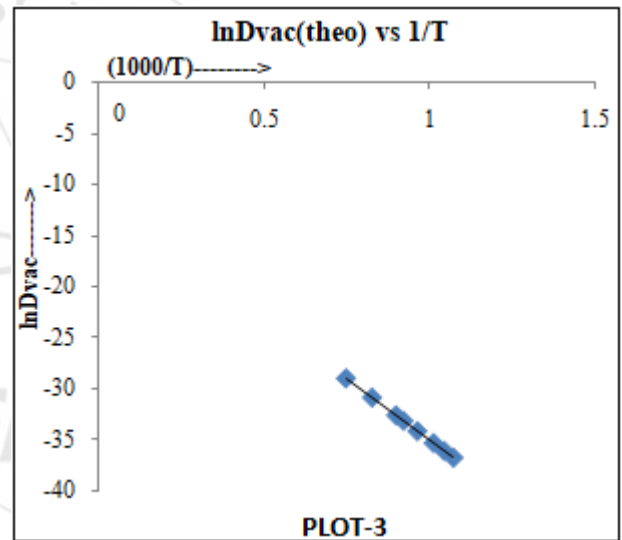
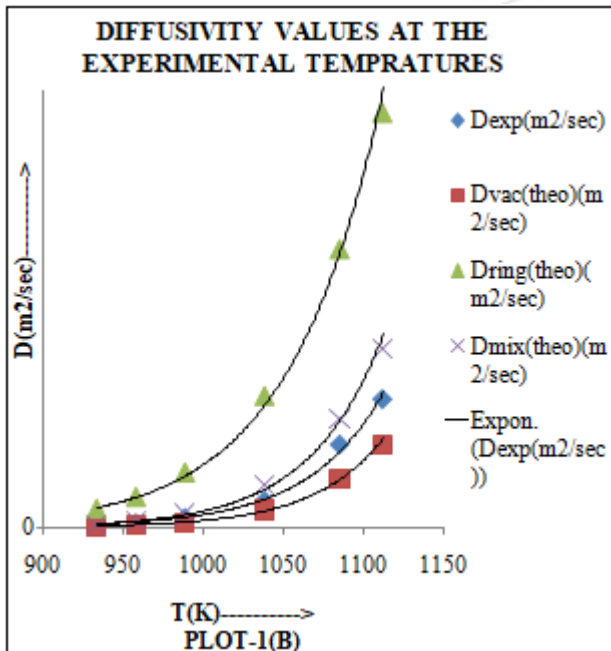
Table 2

$\Delta D/D\%$ (VAC)	$\Delta D/D\%$ (ring)	$\Delta D/D\%$ (mix)
65.47399038	25.75465793	4.654891504
53.66491786	56.97161385	20.09276995
54.89225932	72.01563306	29.71300227
70.55276588	73.05009589	25.1824753
49.53954811	81.62798325	37.9054728
71.27685515	84.28847274	32.43336344
74.13658305	86.86353619	33.19682978
129.2382187	85.35229599	13.82212442

3. Following are the plots of the diffusivity data vs. the experimental temperatures.



The experimental activation energy is calculated from the slope of this Arrhenius plot as 192.8922 KJ/mol

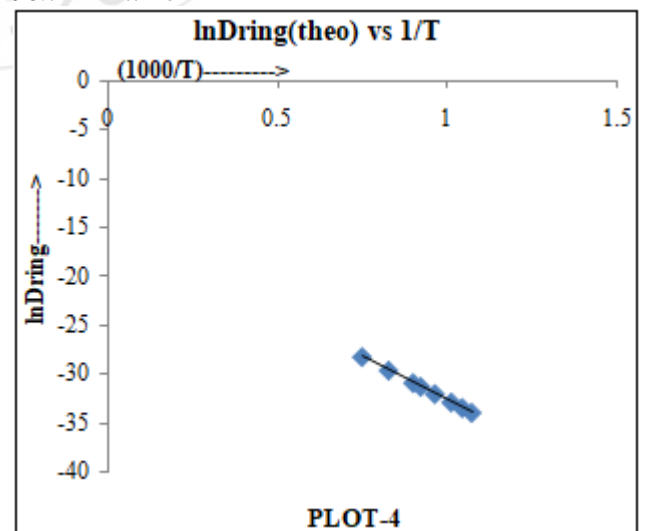


The theoretical activation energy (for vacancy mechanism) is calculated from the slope of this Arrhenius plot as 198.7122 KJ/mol

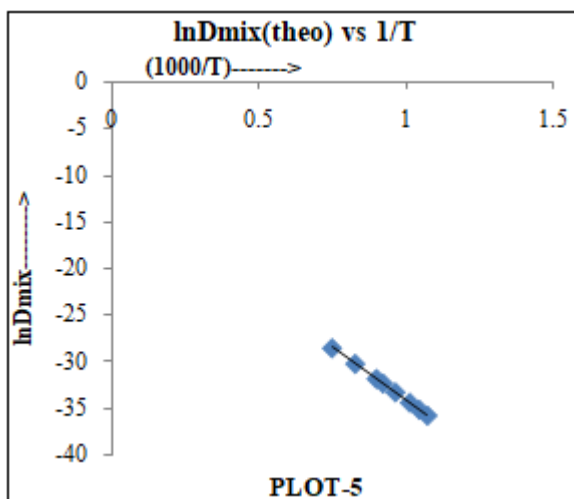
(Plot-1(A) takes all the 8 data points and Plot-1(B) contain the 6 lower temperature data points i.e. from 1112.15K to 933.35K) as these points have become eclipsed in Plot-1(A))

Legend : (Dexp: experimental diffusivity data, Dvac: theoretical diffusivity data for vacancy mechanism, Dring: theoretical diffusivity data for ring mechanism, Dmix: theoretical diffusivity data for mixed (ring cum vacancy) mechanism).

3. Following are the Arrhenius plot of LnD vs. 1000/T



The theoretical activation energy (for ring mechanism) is calculated from the slope of this Arrhenius plot as 148.57688 KJ/mol.



The theoretical activation energy (for mixed (ring cum vacancy) mechanism) is calculated from the slope of this Arrhenius plot as 185.74189 KJ/mol.

Legend: (Dexp: experimental diffusivity data, Dvac: theoretical diffusivity data for vacancy mechanism, Dring: theoretical diffusivity data for ring mechanism, Dmix: theoretical diffusivity data for mixed (ring cum vacancy) mechanism).

4. Looking at table-2 it can be seen that the %deviation of the experimental diffusivity data is least from that of the theoretical diffusivity data value of the mixed (ring cum vacancy) diffusion mechanism. Furthermore closely looking at those deviations especially at lower temperatures, the %deviation for vacancy mechanism is as high as 129.24% at 933.35K and on the other hand the %deviation for mixed mechanism is just 13.822% at the same temperature. This trend is not surprising as the decrease in the vacancy concentration with decrease in temperature (according to equation 5) makes it important for the diffusing atoms to take an alternating pathway (more precisely an alternative mechanism) for diffusion from higher chemical potential to lower chemical potential. The closeness of experimental diffusivity data with that of the theoretical diffusivity data of mixed (ring cum vacancy) mechanism (especially at lower temperatures) advocates the fact that the mixed (ring cum vacancy) diffusion mechanism can be an alternate mechanism of self diffusion.

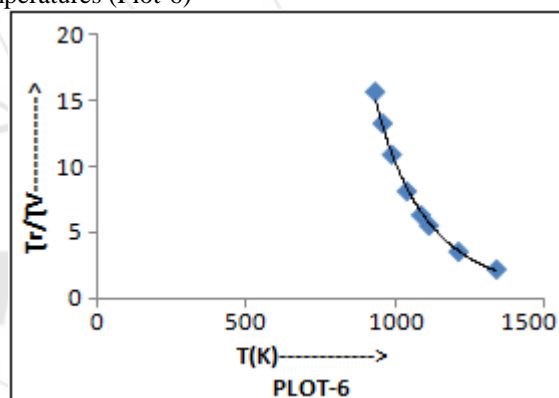
5. The activation energy for mixed (ring cum vacancy) mechanism is consistent with that of the experimental activation energy (although the activation energy for vacancy mechanism is also consistent with that of the experimental activation energy but the large deviation of experimental diffusivity data from that of diffusivity data of vacancy mechanism makes the mixed mechanism the better choice for self diffusion in copper).

6. The value of $\frac{\tau_r}{\tau_v}$ is also calculated at the experimental temperatures (Kelvin) and is shown in table 3 (τ_r : the number of successful jumps per second executed by an atom in ring diffusion mechanism (during ring rotation), τ_v : the number of successful jumps per second executed by an atom in vacancy mechanism (jump into vacancy))

Table 3

T(K)	τ_r/τ_v
1336.15	2.228745747
1209.85	3.571245209
1112.15	5.534956702
1085.35	6.328511048
1038.35	8.139528184
988.65	10.90134984
957.95	13.25597098
933.35	15.65011271

A plot of $\frac{\tau_r}{\tau_v}$ is made against the experimental temperatures (Plot-6)



The curve fitting of the above data shows the relationship as $\frac{\tau_r}{\tau_v} = 2 * 10^{17} T^{-5.45}$ (T is absolute temperature). This kind

of relationship means that with decrease in temperature $\frac{\tau_r}{\tau_v}$ value will increase which means that at lower temperatures τ_r i.e. the number of successful jumps in ring rotation will increase. Again, this trend is not surprising and in turn it reaffirms the fact that with the decrease in temperature (which causes the decrease in vacancy concentration) the atoms are not diffusing through a pure vacancy mechanism and in turn are choosing an alternative mechanism for self diffusion at the lower temperatures.

6. Conclusion

- 1) The vacancy mechanism of diffusion is not the only principal mechanism driving self-diffusion in pure FCC metals especially at lower temperatures where the vacancy concentration is very less.

- 2) Although the vacancy mechanism will not be the sole mechanism for self diffusion in pure FCC metals (at lower temperatures) it will be a member of yet another mechanism which is a conjoint of vacancy and ring diffusion mechanism (named in this paper as the mixed diffusion mechanism)
- 3) This mixed diffusion mechanism (a mechanism which incorporates in itself both ring rotation and vacancy jump) will be the alternative mechanism for the diffusion of atoms in pure FCC metals (especially at lower temperatures).

7. Compliance with Ethical Standards

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- 2) Conflict of Interest: The author declares that he has no conflict of interests.

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Author Profile



Gaurav Kumar is a 3rd year B.Tech student from the Department of Metallurgical and Materials Engineering, National Institute of Technology Durgapur.