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"Reason for Higher Rate of Gas Flow per unit Cross –

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Sectional Area of Smaller Pore Aperture"

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5 **ABSTRACT**

Objectives: The objectives of this research are to 1) Formulate equation that shows the effect of pore aperture (or confinement) on not just the mass movement of molecules but the movement of individual molecules and 2) elucidate the derived equation and illustrate with diameter of pipes or tubes in literature.

Place and Duration of Study: Department of Chemistry and Biochemistry, Research Division, Ude International Concepts LTD (862217), B. B. Agbor, Delta State, Nigeria; Owa Alizomor Secondary School, Owa Alizomor, Ika North East, Delta State, Nigeria. The research started between 2011 and 2013 and discontinued until March, 2018.

Methods: Theoretical and calculational.

Results: The results reaffirm that higher volume of gas flows through pore aperture of longer diameter than shorter diameter. The same is applicable to longer tubes. The velocity of flow (volume of gas diffusing per cross – sectional of pore aperture per unit time) is higher for shorter diameter of pore aperture than longer diameter of pore aperture. The converse is the case for the entropy implicit in the flow of gas through pores of different diameter.

Conclusion: The "reduced velocity" is inversely proportional to the cube root of the diameter of the pore. The entropic value arising from the effect of diameter is directly proportional to natural logarithm of the square of half of the diameter. If the diameter of the pore is equal to the dB wavelength the gas molecule may continue its motion at a root mean square velocity.

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10 **1. INTRODUCTION**
11
12   The kinetic energy of gases is well known, and the velocity of any gaseous particle in gas

13 phase at 273.15 K and above can be determined without much consideration for forces of interaction

14 that promotes a departure from ideality. Gas molecules do not have restricted motion, movement

15 being in any direction. What seems to be ignored is the effect of gravity within the very strong

16 gravitational field of the earth unlike in the moon where astronauts float almost randomly due to weak

17 gravitational field force. In the absence of concentration gradient (chemical potential gradient) or

18 pressure gradient, the random motion of gas molecules is due not only to collision between

19 molecules, but to the weak gravitational attraction for each molecule. This helps in the distribution of

20 gases in all direction in a three dimensional space (3 – D space). The additional implication is that

21 more time could be spent before a gas molecule in gas phase reaches a specific target, though the

22 root mean square velocity remains quantitatively the same. However, according to Simpkins and

23 Williams [1], Brown and Escombe [2], observed that pipes of smaller uniform cross-section deliver

24 gases at a higher rate measured in unit of volume per unit cross – sectional area per unit time than

25 pipes of larger uniform cross-section. It is presumed however, that all pipes were in contact with

26 carbon (II) oxide (CO_2) in a vessel at the same temperature and pressure.

27   Mere fact that gas molecules diffuse from the region of higher concentration to lower

28 concentration does not preclude randomness in the motion of the molecules because of weak

29 gravitational attraction for the molecules by the earth. But the randomness is far more pronounced in

30 open space at zero concentration gradient. It is suggested that confinement or restriction in the space

31 available for the diffusion of gases may reduce randomness. The effect of confinement or restricted

32 space on the diffusion of gases has been studied in different ways [3, 4]. Etienne et al [3], Burada et

33 al [4], and Martens [5] expressed concern for the entropic effect of confinement on the motion of

34 particles; Chow and Skolnick [6] investigated the effect of confinement which entails slowing down of

35 particle motion in cellular medium in particular. The effects of confinement and crowded biological

36 environment on the diffusion of biomolecules have been studied earlier [6 – 9]. Although some highly

37 technical terms and much higher mathematics in particular that are poorly understood may have been

38 used in some research papers [4], but useful information can be obtained. For instance, "in

39 fluorescence correlation spectroscopy (FCS) analysis it is generally assumed that molecular species

40 diffuse freely in volumes much larger than the three-dimensional FCS observation volume. However,

41 this standard assumption is not valid in many measurement conditions, particularly in tubular

42 structures with diameters in the micrometer range, such as those found in living cells (organelles,

43 dendrites, *etc*) and microfluidic devices (capillaries, reaction chambers *etc*)"[3].

44   In the application of Einstein equation, the time it may take a particle in gas phase or in

45   solution and intra-cellular medium is often given as $x^2/2D$ where the parameters, x and D, are the

46   root mean square distance (displacement) and diffusion coefficient respectively. However, the long

47   dimension length of the cell or vessel containing reaction mixture components is not equal to root

48   mean square displacement. This is so because the equation is formulated based on mass diffusion of

49   molecules such that average displacement cannot be attributed to any single molecule; each

50   molecule may cover distance different from distance covered by any other molecule. Given specified

51   condition for the determination of D, the root mean square distance, x can be correctly determined for

52   a given time, t. In other words, the parameter x is a function of t, and not the other way round. Thus

53   within the mass movement of molecules along concentration or pressure gradient individual

54   molecules retain its velocity influenced by potential energy intrinsic in the concentration or pressure

55   gradient and thermal energy. This is to suggest that single molecule motion can be tracked

56   instrumentally. Single-particle tracking (SPT) methods with hi-tech instrumentation are, according to

57   Michalet [10] and references therein, widely used for the study of microscopic behaviour and

58   interactions of individual molecules or microscopic objects in soft matter and biological environment.

59   Based on kinetic theory of matter, the root mean square velocity of gas molecule in free space is

60   established. From point "a" to point "b" the distant apart may be » the long dimension length of the

61   molecule such that the molecule may not move in only one direction. Therefore, if the distance apart

62   is say, l the latter divided by the total time spent in all direction in random motion should be < the root

63   mean square velocity. It is speculated that randomness is minimized in confined space such as space

64   within the tube. In this regard, more than 100 years ago Brown and Escombe [2] observed that pipes

65   of narrower diameter delivers carbon dioxide at higher rate in volume per unit cross section per unit

66   time than pipes of wider diameter. There seem not have been any precise reason for this observation

67   and any other observation by contemporary investigators [3, 5]. Therefore, the objectives of this

68   research are to 1) Formulate equation that shows the effect of pore aperture (or confinement) on not

69   just the mass movement of molecules but the movement of individual molecules and 2) elucidate the

70   derived equation and illustrate with diameter of pipes or tubes in literature.

71   **2.0   Formulation of Mathematical Model**

72   This section concerns the formulation of the fundamental model which begins with following

73   equation.

74
$$u = \frac{v}{n} \qquad (1)$$

75 Where *v* and *u* are the root mean square (r m s) velocity and "reduced velocity" (otherwise called

76 "pseudo-velocity"), respectively, and, *n* is » 1 due to time spent in other directions other than the

77 preferred direction in a straight line. This view is similar to the analogy expressed in literature. The

78 difference however, is that the diffusion of solute facing obstacles in fluid phase including intracellular

79 environment is the case as described by Kao et al [11]. The time required for an auto to reach a target

80 destination depends on its speed, the fraction of time it is in constant motion, and its route. This is to

81 say there may not be direct straight course to preferred destination. Continuous motion of an

82 automobile at constant speed is analogous to not only fluid-phase solute diffusion [11], but to the

83 diffusion or random displacement of gas molecules driven by thermal energy.

84 The main principle upon which this derivation is based is de Broglie principle (dB). Therefore,

85 apply dB and obtain:

86
$$m \left(\frac{v}{n} \right)^2 = h f_{\mathrm{dB}(1)} \qquad (2)$$

87 Where $f_{\mathrm{dB}(1)}$ is the reduced dB frequency, *m* is the mass of a molecule and h is the Planck's constant.

88 Accordingly, there should be increased dB wavelength ($\lambda_{\mathrm{dB}(1)}$). These parameters, decreased $f_{\mathrm{dB}(1)}$ and

89 increased $\lambda_{\mathrm{dB}(1)}$ are regarded as pseudo-quantities in contrast to the real quantities expected if the

90 total distance in all directions as against the preferred single direction to the target destination, is

91 divided by the total time. From Eq. (2),

92
$$f_{\mathrm{dB}(1)} = f_{\mathrm{dE}}/n^2 \qquad (3)$$

93 Equation (3) arises because $mv^2 = h f_{\mathrm{dB}(1)} n^2$ and $h f_{\mathrm{dB}(1)} n^2 = h f_{\mathrm{dB}}$ where f_{dB} is the dB frequency at r

94 m s velocity, *v*.

95 Meanwhile,

96
$$(mu)^2 = \left(\frac{h}{\lambda_{\mathrm{dB}(1)}} \right)^2 \qquad (4)$$

97 Where $\lambda_{\mathrm{dB}(1)}$, is the pseudo-wavelength applicable to reduced velocity (or pseudo-velocity). From Eq.

98 (4),

99
$$u^2 = \left(\frac{h}{m \lambda_{\mathrm{dB}(1)}} \right)^2 \qquad (5)$$

100 Since $\left(\frac{v}{n} \right)^2 = u^2$, then, $\left(\frac{v}{n} \right)^2 = \left(\frac{h}{m \lambda_{\mathrm{dB}(1)}} \right)^2$ and so,

101
$$\lambda_{dB(1)} = \frac{nh}{mv} \tag{6}$$

102 Besides, $\lambda_{dB} = \frac{h}{mv}$. Hence,

103
$$\lambda_{dB(1)} = n\,\lambda_{dB} \tag{7}$$

104 Where λ_{dB} is the dB wavelength at r m s velocity, v. As long as Eq. (1) holds, then,

105
$$n = d_0/d \tag{8}$$

106 Where d_0 (or $v\,t$) and d ($u\,t$) are the total distance covered in every direction and the distance covered

107 in the real direction on a straight course (*i.e.* along preferred straight route) respectively in time, t.

108 Meanwhile,

109
$$v/n = \lambda_{dB(1)}f_{dB(1)} \tag{9}$$

110 Thus,

111
$$v \text{ or } \frac{d_0}{t} = n\lambda_{dB(1)}f_{dB(1)} \tag{10}$$

112 From Eq. (10),

113

114
$$\lambda_{dB(1)} = d_0/n\,f_{dB(1)}t \tag{11}$$

115 However, $mu = h/\lambda_{dB(1)}$ and so, substitution of $\lambda_{dB(1)} = h/mu$ into Eq. (11) gives:

116
$$u = nhf_{dB(1)}t/md_0 \tag{12}$$

117 Meanwhile multiply both side of Eq. (12) by n and obtain:

118
$$nu(\text{or } v) = n^2 hf_{dB(1)}t/md_0 \tag{13}$$

119 There should be a time $t_x(t_x \neq t)$ such that $f_{dB(1)}t_x = n$. Therefore, if D_0 is the total distance covered

120 in all directions in t_x, at r m s velocity, v, then,

121
$$D_0 = n^3\lambda_{dB} \tag{14}$$

122 Equation (14) arises as follows: In place of t in Eq. (13) t_x is used while in place of d_0, D_0 is used;

123 since $h/mv = \lambda_{dB}$, then when D_0 is made the subject of the formula, Eq. (14) remains as it is.

124 Keeping the relationship between u and v in mind, and as long as Eq. (14) holds, then,

125
$$D_1 = n^2\lambda_{dB} \tag{15}$$

126 where D_1 is the distance measured in a single straight line towards the preferred destination in t_x. So,

127
$$D_0 = n^2\lambda_{dB(1)} \tag{16}$$

128 Equation (16) arises because $\lambda_{dB(1)} = n\lambda_{dB}$ and,

129
$$D_1 = n\lambda_{dB(1)} \tag{17}$$

130   Note that the above equation arises because, the dB wavelength (λ_{dB}) at v is shorter than the

131   wavelength ($\lambda_{dB(1)}$) at u while the total distance (D_0) covered in all directions in a random motion in

132   time, t_x at v is always longer than D_1.

133   In Eq. (13), $f_{dB(1)} = u/\lambda_{dB(1)}$ and so,

$$v = hn^2ut/md_0\lambda_{dB(1)} \tag{18}$$

135   Substitution of Eq. (12) into Eq. (18) gives:

$$v = h^2n^3t^2f_{dB(1)}/m^2d_0^2\lambda_{dB(1)} \tag{19}$$

137   In Eq. (19), $D_0/t_x = d_0/t = v$. So,

$$v = h^2n^3t_x^2f_{dB(1)}/m^2D_0^2\lambda_{dB(1)} \tag{20}$$

139   In Eq. (20) $n^3f_{dB(1)}$ stands for nf_{dB} $(i.e.\, n(n^2f_{dB(1)}) = nf_{dB})$ and if Eq. (16) is squared the result can

140   be used in place of D_0^2 in Eq. (20) so that,

$$v = h^2t_x^2f_{dB}/m^2n^3\lambda_{dB(1)}^3 \tag{21}$$

142   Yet, $f_{dB} = v/\lambda_{dB}$ and so, Eq. (21) becomes:

$$v = h^2t_x^2v/m^2n^3\lambda_{dB}\lambda_{dB(1)}^3 \tag{22}$$

144   Keeping in mind that D_0 is the same as $n^3\lambda_{dB}$ and making appropriate substitution into Eq. (22), and

145   after rearrangement, the result is:

$$m^2\lambda_{dB(1)}^3D_0 = h^2t_x^2 \tag{23}$$

147   Therefore,

$$\lambda_{dB(1)}^3 = h^2t_x^2/m^2D_0 \tag{24}$$

149   From Eq. (24),

$$\lambda_{dB(1)} = \sqrt[3]{\frac{h^2t_x^2}{m^2D_0}} \tag{25}$$

151   Nonetheless, $\lambda_{dB(1)} = h/mu$ and substitution into Eq. (25) gives:

$$h/mu = \sqrt[3]{\frac{h^2t_x^2}{m^2D_0}} \tag{26}$$

153   Making u in Eq. (26) subject of the formula gives:

$$u = \frac{h}{m}\sqrt[3]{\frac{m^2D_0}{h^2t_x^2}} \tag{27a}$$

155   But $t_x^2 = D_0^2/v^2$ and $v^2 = 3k_B\theta/m$ such that substitutions into Eq. (27a) give:

$$u = \sqrt[3]{\frac{3k_B\theta h}{m^2D_0}} \tag{27b}$$

157   Equation (27b) is subject to analysis in the results and discussion section.

158   **2.1   Derivable equation of entropy arising from random motion of gases**

159   Given that the rate of flow or flux per cross-sectional area through a given pore of known diameter is:

160     $R_v/\pi r^2$, then,

$$u = \sqrt[3]{\left(\frac{3k_B\theta h}{m^2 n^3 \lambda_{dB}}\right)} = R_v/\pi r^2 \tag{28}$$

162   Where, r and R_v are the radius of the pore and rate of gas flow in volume per unit time respectively.

163   There is need to add that if X volume of a gas diffused through a pipe in time t, regardless of length,

164   the total distant along the length of the pipe whose uniform cross-section is known is (X/cross-

165   sectional area)/.t. In Eq. (28), $n^3\lambda_{dB}$ takes the place of D_0 defined in Eq. (14). Making n^3 subject of the

166   formula gives:

$$n^3 = \left(\frac{\pi r^2}{R_v}\right)^3 \frac{3k_B\theta h}{m^2 \lambda_{dB}} \tag{29}$$

168   Replacing λ_{dB} in Eq. (29) with $h/\sqrt[2]{3mk_B\theta}$ gives after rearrangement:

$$n^3 = \left(\frac{\pi r^2}{R_v}\right)^3 \left(\sqrt[2]{\frac{3k_B\theta}{m}}\right)^3 \tag{30}$$

170   If volume ($V_{(1)}$) swept out in specific direction is given as $V_{(1)} = A\,n^2\lambda_{dB}$ where A is the cross –

171   sectional area and if the volume (V) swept out in multiple directions in random motion is given as

172     $V = A\,n^3\lambda_{dB}$, then $\frac{V}{V_{(1)}} = n$. Therefore, the entropic expression is:

$$\Delta S = R\ln n$$

$$\Delta S = R\ln\left(\frac{\pi r^2}{R_v}\sqrt[2]{\frac{3k_B\theta}{m}}\right) \tag{31}$$

175   At the earliest part of diffusion through the pore the rate of flow or diffusion in terms of volume

176   per cross-sectional area of pore per unit time, is given by Eq. (27) or Eq. (28) where D_0.is replaced by

177   the diameter of the pore. The earliest rate of diffusion (R_{vE}) otherwise called conductance through the

178   pore in terms of volume per unit time is therefore given as:

$$R_{vE} = \pi r^2 . \sqrt[3]{\frac{3K_B\theta h}{m^2 D_0}} \tag{32}$$

180   Substitution of Eq. (32) into entropy equation, Eq. (31) (the replacement of R_v with R_{vE}), gives after

181   rearrangement the equation of entropy at the earliest stage of diffusion through the pore.

$$\Delta S = R\ln\left(\left(\sqrt[6]{3mk_B\theta}\right).\sqrt[3]{\frac{d_{ia}}{h}}\right) \tag{33}$$

183   where d_{ia} is the diameter of pore.

184   The advantage of transport of particles through restricted channels in fluid medium and pores

185   has been put to god use. For instance, the advent of nanotechnology has its application in civil

186   engineering (effectively dispersing engineered nanomaterials in fiber-reinforced composites during

187   processing involves transport through a polymer solution or melt as well as through the rigid fiber

188   network) and medicine (delivering drugs, diagnostics, or therapeutic agents to targeted tissues in the

189   human body requires transport through the rigid extracellular matrix and the extracellular fluid volume

190   or through the highly selective blood–brain barrier) [7]. The issue is that nanoparticles move through

191   pores or spaces that are not less than nano-scale size. It is obvious therefore, that the issue of pore

192   size is very important or has very useful application in both biological and physical processes. But it is

193   not yet known if pore size or extra – or intra – cellular space is shorter than nano – scale length.

194   Porous structures (metal – organic framework materials), possessing big surface area, have potential

195   application as novel adsorbents and catalysts [12]. Possible use for greenhouse gases removal,

196   hydrogen storage for future clean energy technologies, and for highly selective separation of gaseous

197   mixtures has according to Sartowska *et al* [12] and references therein been the motivation for the

198   interest in porous structures. Construction at the nanometre length scale of porous materials which

199   may be needed at present, for many potential applications has been proposed by Sartowska *et al* and

200   references therein [12]. Although the fluid media as can be found in extra – or intra – cellular medium,

201   presents different hydrodynamic environment from gas phase, both media have one thing in common

202   and that is just diffusion phenomenon. However, in support of the difference in rate of diffusion

203   between fluid medium and gas phase, is the observation that the diffusion of dye molecules being

204   confined in single conical nanopore channels is slower than that in the bulk solution [13] unlike the

205   report by Brown and Escombe [2]. Whatever be the case, it is not certain yet if a pore size or

206   intermolecular space within the cell in particular or through the membrane can be as short as the dB

207   wavelength of the smallest molecule, the hydrogen molecule let alone larger or heavier molecules.

208   Related to this concern is the discussion on quantum aspects of the center-of-mass motion of

209   complex molecules, *i.e.* on the coherent splitting of their dB wave fronts, their recombination and

210   interference and most importantly the experiments, in which dB wavelengths range between $\lambda_{dB} = h =$

211      $m\,v = 0.3 – 5\exp(−12)$ m, which is typically $10\exp(3) – 10\exp(4)$ times smaller than the size of the

212   molecule itself and comparable to the shortest wavelengths in high-resolution transmission electron

213   microscopy [14]. The implication or effect of radius as short as dB wavelength is to be stated in the

214   results and discussion section.

215   The advantage of pore size has application in domestic kerosene stove where the combustion

216   chamber is surrounded by two perforated cylinders with open ends. The hydrocarbon (HC), kerosene

217   which according to Matveev *et al* [15] contains dozens of various HC components has been the object

218   of intense research with intention of determining ways of obtaining maximum energy value available

219   in it. Its total combustion in Jet engine [15], lantern [16] combustion chamber and use of ethanol –

220   kerosene mixture [17] require sufficient supply of oxygen that can be made possible with device that

221   can reduce randomness like pores with very short diameter ranging from few nanometers to few

222   micrometers.

223   **3.   Methods**

224   The research is mainly theoretical which attempts to derive equations (based on de Broglie

225   principle) that can elucidate qualitatively and quantitatively the reason why narrower apertures allows

226   larger volume of gas diffusion per unit cross-sectional area per unit time than pores of longer

227   diameter. The degree of randomness and cognate entropic parameter where determined by

228   substituting appropriate data in literature to the appropriate equations derived in this research.

229   **4.   Results and Discussion**

230   A series of stepwise derivation based essentially on dB principle – the wave – particle duality

231   – ended in two major equations, Eq. (27b) and Eq. (31). Before, proceeding with the mathematical

232   equation, it is instructive to realize that dB principle seems to be applicable mainly to components of

233   the electromagnetic spectrum as the paper by [14] suggests. Although the issues in the paper by

234   Brand *et al* [14] are not very clear as expected for non-specialist, but they go to illustrate almost the

235   universality in the application of dB theory *vis-à-vis* its application in this research in the elucidation of

236   physico-chemical phenomenon. In other words dB model can be applied to both micro – and macro –

237   particles in motion. This research does not cover diffraction experiment but reference to double – or

238   multiple – split diffraction experiment is intended to support the premise that dB model can apply to

239   almost every particle: According to Brand *et al* [14] and references therein, double – and multi – slit

240   diffraction experiments with massive matter have been realized with electrons, neutrons, atoms and

241   their clusters, as well as small and large molecules. This issue is therefore, connected to the view that

242   a relationship between physical constants from the microcosms (subatomic world) and the

243   macrocosms (cosmos) plays an important role in physics [18]; this implies that Planck's constant may

244   be "a bridge" between microcosm and macrocosm which seems to be accomplished by writing

245   Newton's gravitational constant as a function of Planck's constant [18]. But there is also a role for

246   Planck's constant in the concept of wave – particle duality in which the particle aspect can best be

247   described as a deterministic property in addition to its description as discrete local particle subject to

248   detection and in which the wave aspect which is probabilistic or stochastic in nature is also described

249   as the indistinguishable delocalized wave nature that explains the interference pattern [14]

250   characteristic of typical wave as observed in double slit experiment. What is relevant is that dB wave

251   length and frequency as used in this research may be justified.

252   At this junction Eq. (27b) and Eq. (28) can be re-examined. If $D_0 \rightarrow \lambda_{dB}$, that is, if $n^3 \rightarrow 1$, $u \rightarrow$

253   v. This can be shown as follows: With $n = 1$, substitution of $h/\sqrt[2]{3mk_B\theta}$ into Eq. (28) expressing u,

254   should give:

255
$$u = \sqrt[3]{\frac{3k_B\theta h.\sqrt[2]{3mk_B\theta}}{m^2 h}} \qquad (34a)$$

256   Taking the cube of Eq. (34a) and simplifying gives:

257
$$u^3 = \left(\sqrt[2]{\frac{3k_B\theta}{m}}\right)^3 \qquad (34b)$$

258   Taking the cube root gives:

259
$$u = \sqrt[2]{\frac{3k_B\theta}{m}} \equiv v \qquad (34c)$$

260   Equation (34c) is very likely because in Eq. (1) $u = v/n$. Consequently $\frac{v}{n} = \sqrt[3]{\left(\frac{3k_B\theta h}{m^2 n^3 \lambda_{dB}}\right)}$; squaring of both

261   sides of the equation, should eliminate n^3 such that re – substitution of $h/\sqrt[2]{3mk_B\theta}$ into the resulting

262   equation reproduces the root mean square velocity, v.

263   The equations, Eq. (27b) and Eq. (28) – the reduced velocity equation – and Eq. (31), the

264   equation of entopic effect were derived so as to quantify the parameters they stand for. However,

265   there are models in literature [19, 20] that may not yield the same results as applicable to the models

266   in this research. Indeed the flow rate of carbon (IV) oxide in volume per hour in particular as reported

267   by Brown and Escombe [2] is « the results (Table 1) obtainable from the use of models such as

268    $C_{mL} = \frac{d^3}{3l}\sqrt[2]{\frac{\pi R_0 T}{2M_m}}$ [20] where C_{mL}, d, l and R_0 are the conductance through long tube of uniform circular

269   cross section, diameter of the tube's orifice, length of the tube and universal gas constant

270   respectively; T and M_m are the thermodynamic temperature and molar mass of the gas respectively.

271   The same scenario also played out when the results (Table 1), that is the values of the conductance

272   of an aperture whose equation is given as $C_a = A . \sqrt[2]{\frac{R_0 T}{2\pi M_m}}$ [20] (where A is the cross – sectional area

273   of aperture) is compared with results from Brown and Escombe [2]. At a glance in Table 1, one sees

274   that all parameters determined by different models, the model in this research and model in literature,

275   were higher with longer diameter (or radius) of the aperture. In Table 2, are parameters generated at

276   the earlier part of diffusion or flow of gas through the aperture of the tube. Expectedly the "reduced

277   velocity" of flow is lower for longer tubes than shorter tubes; but the conductance values were higher

278   for longer tubes than for shorter tubes. Also, the entropic parameters (Table 1 – 3) were higher for

279   longer pore diameter than for shorter pore diameters for tubes in line with the models, Eq. (31) and

280   Eq. (33), in this research. One should also consider the fact that flow at the earlier part is around the

281   thickness of the pore aperture.

282   Table 3 shows the parameters generated at the earlier stage of diffusion through the pore

283   aperture. The conductance, C_a and the entropy, ΔS are higher with longer diameter than smaller

284   aperture unlike the reduced velocity, u. This scenario is what may be prevalent in kerosene stove in

285   which there are two perforated open – ended cylinders, the inner and outer cylinders. The small

286   apertures reduce the random diffusion or more technically the entropy in gas flow thereby

287   concentrating the air/oxygen around the ignited weak soaked in kerosene. A lot have been expressed

288   regarding the combustion of kerosene [15 – 16, 18]. However, it is a commonplace observation that in

289   the absence of perforated cylinders around the combustion chamber or the weak, high degree of

290   luminosity of the flame is the case due to insufficient air supply. But with the perforated cylinders

291   massive supply of air in higher concentration leads to complete combustion that gives bluish flame

292   with much less luminosity.

293   One may recall the fact that the aim of this research is to proffer answer or reason why

294   smaller apertures allows faster rate of gas flow per cross – sectional area per unit time. Equation

295   (27b) seems to explain this observation. But it must be pointed out that there are ways of gas flow

296   such as pure molecular diffusion (in this case there is no contact with the walls of the pore), Knudsen

297   + molecular diffusion (in which there are contacting and non-contacting molecules with the walls of the

298   pore), pure Knudsen diffusion (in which there is total contact or collision with the wall of the pore), and

299   diffusion through "tortuous paths" which occurs in compacted solids [19, 20]. A gas molecule will

300   always deviate from its originally course, as a consequence of randomness which is reduced

301   according to Eq. (27) or Eq. (28). The issue arising from these various ways or mechanism is the

302   negation of one or two of the postulates of the kinetic theory of gases in particular; the fact that gas

303   molecules in the absence of chemical potential gradient or pressure gradient is always in constant

304   random motion colliding elastically with each other and the walls of the vessel cannot be overlooked.

305   One may wish to know the significance of Eq. (27b) or Eq. (28) given Eq. (1). Equation (27b)

306   or Eq. (28) unlike Eq. (1) directly illustrates likely effect of diameter on the rate of diffusion in volume

307   per unit cross – sectional area per unit time. The question is there any capillary whose diameter is of

308   the nano-scale length needs to be answered. This may not be impossible if suitable technology to do

309   so has been contrived similar to suggestion elsewhere [12]. But if in nature, human pulmonary system

310   for instance where the terminal bronchiole diameter may not be as small as nano-scale length, it

311   shows that randomness may not be totally eliminated in bio – and non – biophysical process such as

312   diffusion. As shown in Table 1, there are different values of u for different values of the diameter of the

313   pores if it is assumed that the diameter of the pores is equal to D_0. Indeed the magnitude of u for the

314   same gas is inversely proportional to the cube root of D_0 or diameter, d (which may be = $n_p\lambda_{dB}$ where

315   n_p may be number of times the molecules moved in different directions or degree of randomness.).

316   Thus the values of u decrease as D_0 or d increases, while according Eq. (31) the entropy decreases

317   with decrease in the length of the diameter of the pores (Table 1). Determination of u values and

318   entropy implicit in random motion seem not to have any parallel in literature as in this research which

319   should motivate further research experimentally. But a lot of concern has been expressed in literature

320   without equations that may quantify the parameter as in this research. According to Marten [5] and

321   references therein, there are large variety of natural and artificial confined geometries in which the

322   geometric restriction to the particles' dynamics result in confined diffusion and what is referred to as

323   entropic barrier. While a typical man-made confined geometry may the perforated double cylinders of

324   kerosene stove [18] there are natural confined geometries such as biological cells, membrane ion

325   channels *etc* [5], the bronchioles in lungs, the stomata in plants *etc*. There is a call for the recognition

326   of both Brownian motion and entropic effects whenever study of transport of gases at the macro – and

327   nano – scales through confined geometries is carried out [21] such as stomata, for instance. In gas

328   phase the reduction of randomness or entropy, promotes higher volume of gas flow per cross –

329   sectional area of pore per unit time which is more likely with pore of shorter diameter than pore of

330 longer diameter as shown by the work of Brown and Escombe [2]. The basis of this is illustrated with

331 Eq. (27b) and Eq. (28) in this research and the entropic values are shown in Table 1 – 3. Initially or at

332 earliest stage of diffusion the parameter expressed by Eq. (27b) or Eq. (28) are higher (Table 2) than

333 latter values but much less than latter values with respect to entropic values calculated with Eq. (31).

334 Several authors (researchers to be specific) after Brown Escombe [2] namely Raschk [22], Wong *et al*

335 [23], McElwain and Chaloner [24], Hetherington and Woodward [25], Franks and Beerling [26],

336 MacElwain *et al* [27] cited by Elliott – Kingston *et al* [28] confirms the effect of smaller stomata and

337 consequently small apertures in general. Smaller stomata have > surface area to volume ratio than

338 larger stomata [28]. Before proceeding further, it is necessary to state that this research is not about

339 plant physiology; rather stoma is a good example that exemplifies the effect of the diameter of

340 apertures.

341 It is relevant to point out that within mass movement of molecules, a single molecule

342 translational motion is the focus of model formulation; this is no longer strange as single – particle

343 tracking method with hi – tech instrumentation are used for the study of microscopic behaviour and

344 interactions of individual molecules, microscopic objects in soft matter or biological environment [10].

345 **5. CONCLUSION**

346 The equations that explain the effect of different diameters of conduit pipes which may be

347 biological or non – biological were derived. The reduced velocity is inversely proportional to the cube

348 root of the diameter of the pore. The entropic value arising from the effect of diameter is directly

349 proportional to natural logarithm of the square of half of the diameter. If the diameter of the pore is

350 equal to the dB wavelength the gas molecule may continue its motion at a root mean square velocity.

351 **Table 1. Entropic parameters, conductance of aperture and long cylindrical tube from theory**

352 **and experiment.**

$\Delta S = R\ln\left(\frac{\pi r^{-2}}{Rv}\sqrt[2]{\frac{3k_B\theta}{m}}\right)C_a$ (J/mol.K)(in this research and [])	$\dot{C}a = A.\sqrt[2]{\frac{R_0 T}{2\pi Mm}}$ for aperture (Theoretical) Exp (-3) (m^3/s)[]	B & E $\bar{c}a$ for aperture (Experimental) Exp (-11) (m^3/s) []	$C_{mL} = \frac{d^3}{3l}\sqrt[2]{\frac{R_0 T}{2 M_m}}$ for long tube (Theoretical) Exp (-3)(m^3/s) []	B & E C_{mL} for long tube (Experimental result) Exp (-11) (m^3/s) []
56.95	43.02	6.61	7.722	1.325

55.20	12.14	2.58	1.853	0.35
"	"	2.83	7.722	1.158
53.20	2.87	1.54	6.916	1.079
53.28	3.04	1.74	6.806	1.122
51.55	0.87	1.11	3.847	0.636
51.53	0.86	1.10	3.175	0.569

353 C_a is the Conductance of aperture; C_{mL} is the conductance of long tube. B&E is Brown & Escombe
354 result from experiment; R_0, S, r, R_v and k_B are the gas constant, entropy, radius of pore, rate of flow of
355 gas in volume per unit time, and Boltzmann constant; A, M_m, θ (in this research), T(in literature) area
356 of pore, molar mass of the gas and thermodynamic temperature respectively.
357

358 **Table 2. Entropic parameter, reduced velocity, and conductance of aperture of a long tube.**

Earlier $\Delta_S = R\ln\left(\left(\sqrt[6]{3mk_B\theta}\right).\sqrt[3]{\frac{dia}{h}}\right)$ for a long tube in this research and [] (J/mol.K)	velocity, and $L = \sqrt[3]{\pi\, r^2 l}$ (m)B	Earlier B & E Theoretical u for a long tube in this research and [] (m/s)	Earlier B & E Theoretical $C_a = \pi\, r^2 u$ for a tube in this research and [] (exp (-5) m^3)
57.01	0.0424	0.3972	1.7923
"	0.0682	0.3389	2.8841
"	0.0424	0.3972	1.7923
56.96	0.0435	0.3939	1.7751
56.99	0.0436	0.3935	1.8110
57.02	0.0538	0.3667	2.2968
56.86	0.0522	0.3706	1.9833

359 $C_a = \pi r^2 u = \pi r^2 \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}}; u = \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}};$ Earlier B&E theoretical u means the reduced velocity and other
360 lower parameters at the earliest stage of diffusion through the long tube. The same is applicable to
361 entropy. S; C_a, r, l, and d_{ia} are the entropy, conductance of aperture of a long tube, radius of aperture,
362 length of tube, and diameter of tube; m, R, k_B, h, and θ are mass of the molecule, gas constant,
363 Boltzmann constant, Planck's constant and thermodynamic temperature. Some parameters are
364 theoretically determined in this research.
365
366 **Table 3. Earlier entropic parameter, reduced velocity, and conductance of aperture.**
367

Earlier $\Delta_S = R\ln\left(\left(\sqrt[6]{3mk_B\theta}\right).\sqrt[3]{\frac{dia}{h}}\right)$ for aperture in this research and []	Diameter [] (mm)	Earlier B & E theoretical u for aperture in this research and []. (m/s)	Earlier B & E theoretical $C_a = \pi\, r^2 u$ in this research and [] for aperture exp (- 4) m^3/s

(J/mol.K)			
~56.95	22.7	0.489	1.98
55.20	12.06	0.604	0.69
"	"	"	"
53.20	5.86	0.768	0.21
53.28	6.03	0.761	0.22
51.55	3.233	0.936	0.08
51.53	3.216	0.938	~ 0.08

368

369 $C_a = \pi r^2 u = \pi r^2 \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}}$; $u = \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}}$; Earlier B&E theoretical u means the reduced velocity and other
370 lower parameters at the earliest stage of diffusion through the aperture. The same is applicable to
371 entropy. S; C_a, r, l, and d_{ia} are the entropy, conductance of aperture of a long tube, radius of aperture,
372 and diameter of aperture; m, R, k_B, h, and θ are mass of the molecule, gas constant, Boltzmann
373 constant, Planck's constant and thermodynamic temperature. All parameters are theoretically
374 determined in this research.
375
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