Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2014, 3 (4): 1732-1743

(International Peer Reviewed Journal)

A Generalized Molecular Velocity of the Real Gas

Bahjat R. J. Muhyedeen

Department of Chemistry, College of Science, Baghdad University, Baghdad, **IRAQ**

Email: bahjatrj@mass-energy-e-mbc.com

Accepted on 17th July 2014

ABSTRACT

A generalized equation for the molecular velocity of the real gases has been derived from the momentum of a molecule and the thermodynamic parameters viz. temperature, pressure and volume, and number of the moles, which are used to estimate the reaction rate constant in the gas and solution phase in any reaction. The derived generalized molecular velocity is a function of pressure, temperature, volume, number of moles and molecular weight rather than a function of the temperature and molecular weight only. The generalized molecular velocities of sixteen materials were calculated at different T, P, concentration (n/V). The calculated rate constant for a few bimolecular reactions using the generalized molecular velocity GMV is better fitting experiment than that using kinetic theory velocity KTV.

Keywords: Real gas, molecular velocity, generalized molecular velocity, kinetic theory.

INTRODUCTION

The impact driven by the momentum ($\boldsymbol{p = mv}$) of a molecule of real gas in the reactor is a function of the velocity of the molecule, which is affected by the thermodynamic parameters such as temperature T, pressure P, volume V, and number of the moles n of the real gas in the reactor, in addition to other physical properties of the used material. From kinetic theory point of view, this impact is usually expressed in terms of kinetic energy $E_k = \frac{1}{2}mv^2$, which articulates the fact that a moving object can do work on anything it hits. The kinetic energy represents the energy of motion which is called the translational kinetic energy of the mass, to distinguish it from the rotational kinetic energy. The kinetic theory relates the kinetic energy of the non-interacting molecule to its translational energy E_t (or U_t) of the perfect gas as $E_t = \frac{3}{2}RT$, R being the gas constant, to attain the velocity v of the molecule. The probability of a velocity v_i (in one direction, i) is proportional to $e^{-\frac{mv_i^2}{2kT}}$, k being Boltzmann constant, while the probability of a speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, $f(v)$, is proportional to $v^2 e^{-\frac{mv^2}{2kT}}$ (following Maxwell distribution) as shown in literature[1-3].

The probability that a molecule has a speed between v and $v + dv$ is represented by $f(v)dv$, so that its expected value would be:

$$\bar{v} = \int_{0}^{\infty} v f(v) dv \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Substituting the Maxwell distribution, $f(v) = 4\pi[\frac{M}{2\pi RT}]^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$, into Equation (1) we get,

$$\bar{v} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_{0}^{\infty} e^{-\frac{Mv^2}{2RT}} v^3 \, dv \ldots\ldots\ldots\ldots\ldots\ldots. \quad (2)$$

Using the values of the finite integral ($\int_0^\infty x^3 e^{-ax^2} dx = 1/2a^2$) we obtain the mean speed $\bar{v}$ in terms of temperature and the mass m(kg) or the molecular weight M(kg/mol) of the molecule as seen below:

$$\bar{v} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} x \, \frac{1}{2}\left(\frac{2RT}{M}\right)^2 (\mathrm{m/s}) = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} (\mathrm{m/s}) \text{ at SATP} \ldots\ldots \quad (3)$$

i.e. at standard ambient temperature (298.15 K). Equivalently:

$$\bar{v} = B \frac{1}{\sqrt{M}} (\mathrm{m/s})\,;\ \text{where } M \text{ is in} \frac{\mathrm{kg}}{\mathrm{mol}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Where B= 79.45. The details of the derivation of these equations are available in Literature. It is very clear that the kinetic theory KT describes the mean speed $\bar{v}$ of the molecule as temperature-dependent only; while it neglects the pressure, volume and number moles of the real gas in the reactor. Equation (4) does not satisfy the real behavior of the molecule in real industrial environments due to the collision events.

The collision theory, which proposed by Max Trautz and William Lewis in the early 1900's, describes the reaction rate K as a function of the collision number Z (a.k.a. collision frequency, the average number of collisions/(s.m^3)) and the fraction of the molecules ($\Delta n/n$) having the sufficient energy (activation energy, ΔE) to react. The formula for the total collisions frequency Z_{AB} of one molecule of substance A with molecules of substance B is given by[4]:

$$Z_{AB} = \pi\left(\frac{d_A + d_B}{2}\right)^2 N_A N_B \left(\frac{8kT}{\pi\mu}\right)^{1/2} \ldots\ldots. \quad (5)$$

Where d_A and d_B are the diameters of the molecules A and B, while N_A and N_B are the concentrations of molecules A and B and μ is the reduced mass. The rate constant is usually expressed as $k_2 = Ae^{-\Delta E/RT}$. The rate of the reaction K in terms of concentrations and rate constant could be written as follows[4]:

$$= \pi L 10^3 \left(\frac{d_A + d_B}{2}\right)^2 \left(\frac{8RT}{\pi\mu}\right)^{1/2} e^{-\Delta E_o/RT} C^n \ldots\ldots \quad (6)$$

The parameter L is Avogadro number and C is the concentration to power n. The calculated reaction rates are usually higher than the experimental values therefore the steric factor (a.k.a. the probability factor) ρ, was introduced to decrease the rate constant k_2 values (i.e. $k_2 = \rho Ae^{-\Delta E/RT}$). Where A is called a pre-exponential factor and it is temperature dependent while A of Arrhenius' equation is a simple pre-exponential factor temperature independent. In our understanding that the overestimation in the rate of the reaction resulted from the immature of the physical picture, Z_{AB} formula and velocity factor $\left(\frac{8RT}{\pi\mu}\right)^{1/2}$ because it is temperature dependent only while all the reactions affected by the P, V, T and the concentration.

A Generalized Model for Molecular Velocity: As we see that the kinetic theory velocity KTV $\bar{v}$ (or the mean speed) of Equation (4) is a function of temperature T and molecular weight M only and it is independent of the nature of the gas whether it is ideal or real that shows a shortcoming in rate constant. In the industrial processes the key process variables for the three chemical reactors i.e. batch reactor model (batch), continuous stirred-tank reactor model (CSTR), and plug flow reactor model (PFR) are Residence time (τ), Volume (V), Temperature (T), Pressure (P), Concentrations of chemical species (C_1, C_2, C_3, ... C_n), Heat transfer coefficients (h, U) and catalysts[5,6]. The industrial processes usually run at *high pressure, temperature and concentration*. Although most gases obey the ideal gas law to a good approximation when near room temperature and at a moderate pressure, but real gases do not obey the perfect gas law exactly. It is due to the fact that molecules interact with one another due to repulsive forces between them that lead to expansion and attractive forces result in to compression. In previous article we explained the reason behind these forces[1]. Deviations from the ideal gas law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid. At higher pressures one might need a better description. Several equations of state with two or three parameters were developed for this purpose such as[1-5]:Berthelot, Dieterici, Redlich–Kwong, Soave Modification[7] of the Redlich–Kwong, Gibbons–Laughton Modification of the Redlich–Kwong-Soave, Clausius, Peng–Robinson[8],Peng-Robinson-Stryjek-Vera equations of state (PRSV1)[9] and PRSV2[10], Elliott-Suresh-Donohue[11],Wohl, Beattie–Bridgman, Benedict–Webb–Rubin (PWR), Virial[12] and others. All these equations of state do not relate the molecular velocity of the real gases to the thermodynamic parameters.

In this paper we would like to determine the generalized velocity of molecule v of real gas in the reactor with help from the momentum $(\boldsymbol{p} = mv)$concept and the thermodynamic parameters T, P and concentration which is a function of number of moles and volume, i.e., $g(n, V)$ that affects the number of the collisions Z and, finally, the rate of the reaction of the industrial processes. Therefore, we need to describe the momentum $(\boldsymbol{p} = mv)$ of a molecule with a proper function in terms of energy unit first, and then secondly we need to adopt a suitable formula which describes the thermodynamic parameters that affect the momentum.

In previous articles[13-15] we showed that the kinetic energy notion is a virtual concept because the term $E_k = ½mv^2$ of macro systems is a simple mathematical function to describe the momentum of the mass in a unit of energy. It may be written as a modest multiplication of momentum $\boldsymbol{p}$ times the velocity ν as follows: $E = ½mv^2$ should be rewritten as $E = ½mv_1\boldsymbol{v_2}$ or $E = ½\boldsymbol{p}v_2$[14]. The **first** velocity v_1 represents the velocity of the moving mass, which gives the momentum $\boldsymbol{p} = mv_1$; and the **second** velocity v_2 should be considered as ***unit conversion factor*** from momentum units to energy units. This means that the essential issue in this term $E = \boldsymbol{p}$ $(½v_2)$ is the momentum $\boldsymbol{p}$ while the other two factors, i.e., ½ and v_2, are insignificant as they do not have any physical meaning. The factor (½) is constant and v_2 is ***unit conversion factor*** to express the momentum value in joule units. Although several derivations in the literature prove the existence of these two factors which come from the average velocity (for example, $E = Force\ x\ distance = mad = ma\bar{v}t = m\frac{v}{t}\frac{v}{2}t = ½mv^2$), nevertheless they do not have any physical connotation from energy point of view. Consequently, we relate the momentum of the molecule to the thermodynamic parameters. As we stated above, the momentum $\boldsymbol{p} = mv$ of a molecule in gaseous state could be expressed in unit of joule, as $E_k = mvv$, which is directly proportional to the temperature, pressure and inversely proportional with molar concentration C_M, which is a function $g(n, V) = n/V$of

---

[1] The nuclear magneton theory of Mass Quantization -unified field theory, NMT is now used to confirm Mass Quantization in a similar way as Energy Quantization. The quantized mass (the magnetons) creates the quantized energy and not vice versa. The mass in the universe is quantized and is composed of a package of elementary discrete mass particles called magnetons. The structure of the fermion particles and their antiparticles grows hierarchically from these high gravity circular closed quantized packages rings of magnetic dipoles under drastic circumstances in stars. In the outline of this theory, based on Mass Quantization Principle QMP, the NMT suggests that these circular closed quantized packages rings are arranged in a certain way to build the fermion through formation of quantized nmtionic shells. Both the electron and the proton textures have three nmtionic shells 1st K, 2nd L, and 3rd M while the neutron texture has four quantized nmtionic shells 1st K, 2nd L, 3rd M and 4th N. In atomic and molecular media, the net charge from the permanent or the temporary nmtionic field of the electron results in attractive and repulsive forces, known as **van der Waals**, **Keesom**, **Debye and London** dispersion forces[15].

number of moles n and volume V of the real gas[2]. Hence, the momentum is a function $f(T, P, C_M)$ and other physical properties. When the pressure P and the temperature T increase at low concentration, the number of the collisions Z will increase but at high concentrations the collisions Z will decrease and affect the reaction rate. We may express these relations by the following proportionality formula:

$$(mvv)^x \;\; \alpha \;\; \left(\frac{TP}{g(n,V)}\right)^y \; \dots\dots\dots\dots\dots \qquad (7)$$

The term mvv represents the momentum of the molecule in terms of energy unit, while the term $TP/g(n,V)$ describes the thermodynamic parameters that affect momentum $\boldsymbol{p} = mv$. The mass of the molecule m is usually represented by the molecular weight M of the material (kg/mol). The above proportionality can be re-written as follows:

$$(Mvv)^x = \kappa\left(\frac{TP}{c\left(\frac{n}{V}\right)}\right)^y \; \dots\dots\dots \qquad (8)$$

Solving this equation, for the generalized velocity, can be based on the unit homogeneity, i.e., using dimensional analysis concept, which concludes that meaningful laws should be homogeneous in their units[16]. Noting that on the right-hand side the energy unit is raised to a power x, while the left side quantity raised to power y. To obtain the generalized molecular velocity GMV v in unit m/s we have to set $x = 2, y = 1$, and the proportionality constant κ equals to the gas constant, R=8.31441J/K.mol.

The pressure P, temperature T volume V and n units are in Pa, Kelvin, m^3 and moles respectively. The GMV v in the gaseous state in the reactor after rearrangement can be written as follows:

$$v = \left(\frac{RTPV}{n}\right)^{1/4} * \frac{1}{\sqrt{M}}\,(\mathrm{m/s}) \dots\dots\dots\dots\dots\dots\dots \qquad (9)$$

Equation (9) states that the GMV v is proportional to ¼ power of temperature, pressure, volume, and inversely proportional to the square-root of molecular weight M and number of moles; hence, it is totally different from KTV $\bar{v}$ of Equation (4). The GMV v at SATP, is given as follows (where $n = 1$, $P =$ 101325Pa, $V=$ 0.001m^3, T= 298.15 K, M (kg/mol)):

$$v = (8.31441 * 298.15 * 101325 * 0.001)^{1/4} * \frac{1}{\sqrt{M}}\frac{\mathrm{m}}{\mathrm{sec}} \text{ at SATP} \dots\dots\dots\dots \qquad (10)$$

Or:

$$v = B\frac{1}{\sqrt{M}}\frac{\mathrm{m}}{\mathrm{sec}} \dots\dots.. \left(\text{where } M \text{ is in} \frac{\mathrm{kg}}{\mathrm{mol}}\right) \quad \text{at SATP} \dots\dots\dots \qquad (11)$$

Where B = 22.3842. Hence, the GMV v varies with $T, P, conc.$ (V and n). Equation (9) has the same mathematical behavior as Equation (4), where both of them follow the same power function; i.e. $v = B * M^{-0.5}$ m/s. But the value of B of Equation (4) is temperature-dependent only, while the value of B in Equation (9) is dependent on four terms: T, P, n, V. The GMV v in Equation (9) has been applied to sixteen materials at different pressures, temperatures and number of moles to investigate the difference between GMV v values and KTV $\bar{v}$ values. Plotting the values of GMV v versus the molecular weights gives a power curve with correlation coefficient equal to one (R^2 = 1). Where R^2 is the square of Pearson product-moment correlation coefficient, **PPMCC** or simply **PCC,** which is the measure of the linear correlation between the GMV v and the molecular weights.

---

[2] This is a general rule for the calculation of kinetic energy from any moving mass in macro system. In quantum mechanics, regarding the $E = mc^2$ (re-written as $E = mc_1c_2$, or $E = \boldsymbol{p}c_2$), where the correct visualization and understanding to this equation is supposed be realized in the same way that explained for the kinetic energy above, ***in which c_2 is a unit conversion factor, but not c^2as Einstein perceived***. This means that the energy equation supposed be interpreted as $\boldsymbol{p}$ times c and not m times c^2. The principle of conversion of a mass to energy or vice versa is untenable. This new understanding leads to the *mass-energy conformity principle;* which is part of the novel nuclear theory presented in my paper[15].

RESULTS AND DISCUSSION

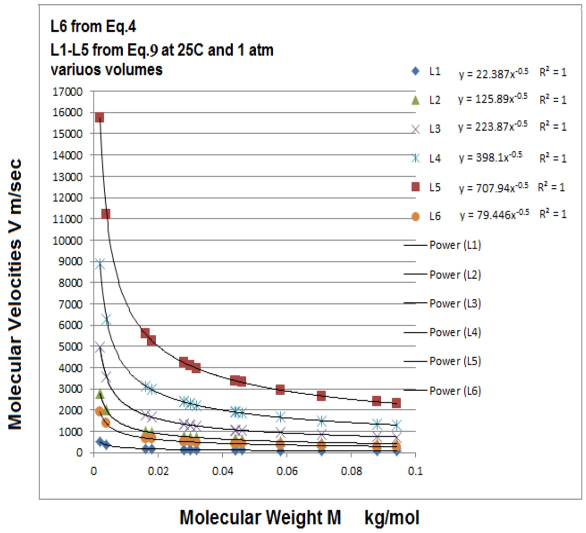
First Trial: Tested at several volumes and pressures**.** We have calculated the GMV v for 16 materials at five volumes starting with pilot reactor (V_1=0.001, V_2=1, V_3=10, V_4=100 and V_5=1000 m^3; each volume is represented by a corresponding line i.e. L_1 and so on), at two pressures (P_1=1 atm, P_2=10 atm), two temperatures (T_1=298.15 ^oK, T_2=373.15 ^oK) and 1 mol. The results are compared with results from Equation (4) as seen in the first column in table 1. Figures 1-4 show that only the curve of the GMV v of L_2 (Line No.2, at V_2=1 m^3, v=126$M^{-0.5}$) comes closer to the KTV $\bar{v}$ of L_6 (Line No.6, which follow eq. 4, v=86$M^{-0.5}$). The GMV v is also calculated at one pressure (P_1=5 atm), two temperatures (T_1=298.15 ^oK, T_2=373.15 ^oK) and $n = 5$ mol as seen in table 2. Only L_2 (at V_2=1 m^3) v = 84.2$M^{-0.5}$ comes closer to L_6 v = 88.98$M^{-0.5}$.

Table 1: The GMV v and KTV $\bar{v}$ values at P=1&10 atm, T=298.15&373.15 ^oK, n=1, V_1-V_5

Materials	Eq.4	Eq.9; P_1=1 atm, P_2=10 atm, T_1=298.15 ^oK T_2=373.15 ^oK, n=1 mol, V_1-V_5=0.001,1,10,100,1000 m^3				
	L_6,T_1/ T_2	L_1, V_1 T_1:P_1/P_2 T_2:P_1/P_2	V_2 T_1:P_1/P_2 T_2:P_1/P_2	V_3 T_1:P_1/P_2 T_2:P_1/P_2	V_4 T_1:P_1/P_2 T_2:P_1/P_2	V_5 T_1:P_1/P_2 T_2:P_1/P_2
H_2	2502 2891	499/887 536/953	2804/4986 3014/5360	4986/8866 5360/9531	8866/15766 9531/16948	15766/28036 16948/30139
He	1776 2052	354/629 380/676	1990/3538 2139/3804	3538/6292 3804/6764	6292/11188 6764/12028	11188/19896 12028/21389
CH_4	887 1025	177/314 190/338	994/1767 1068/1900	1767/3143 900/3378	3143/5589 3378/6008	5589/9938 6008/10684
H_2O	837 967	167/297 179/319	938/1668 1008/1793	1668/2966 1793/3188	2966/5274 3188/5669	5274/9378 5669/10082
CO	671 776	134/238 144/256	752/1337 809/1438	1337/2378 1438/2557	2378/4230 2557/4547	4229/7521 4547/8085
N_2	671 776	134/238 144/256	752/1337 808/1438	1337/2378 1438/2557	2379/4230 2557/4546	4229/7521 4546/8085
NO	649 749	129/230 139/247	727/1292 781/1389	1292/2298 1389/2470	2298/4086 2470/4393	4086/7267 4393/7812
C_2H_6	648 749	129/230 139/247	726/1291 780/1388	1291/2296 1388/2468	2296/4082 2468/4388	4082/7259 4388/7804
O_2	628 726	125/223 135/239	704/1251 756/1345	1251/2225 1345/2392	2225/3957 2392/4254	3957/7037 4254/7565
CO_2	536 619	107/190 115/204	600/1067 645/1147	1067/1897 1147/2040	1897/3374 2040/3627	3374/6000 3627/6450
C_3H_8	535 618	107/190 115/204	600/1066 644/1146	1066/1896 1146/2038	1896/3371 2038/3624	3371/5994 3624/6444
NO_2	524 605	104/186 112/200	587/1044 631/1122	1044/1856 1122/1995	1856/3300 1995/3548	3300/5869 3548/6309
C_4H_{10}-n	466 539	93/165 100/177	522/928 561/998	929/1651 998/1775	1651/2936 1775/3156	2936/5221 3156/5613
Cl_2	422 488	84/150 90/161	473/840 508/902	840/1495 904/1607	1495/2658 1607/2858	2658/4727 2858/5082
$C_5H_{11}OH$	378 437	75/134 81/144	424/754 456/810	754/1340 810/1441	1341/2384 1441/2563	2384/4240 2563/4558
C_6H_5OH	366 423	73/130 78/139	410/730 441/784	730/1298 784/1395	1298/2307 1395/2480	2307/4103 2480/4411
Ratio $v/\bar{v}$ @T_1:R_{P1}/R_{P2} @T_2:R_{P1}/R_{P2}		0.28/0.50 0.27/0.47	1.59/2.82 1.50/2.66	2.82/5.01 2.66/4.74	5.01/8.91 4.74/8.43	8.91/15.84 8.43/14.98

Tabel 2: The GMV υ and KTV $\bar{\upsilon}$ values at P=5 atm, T=298.15&373.15 °K, n=5, V_1-V_5

Materials	Eq.4	Eq.9; P=5 atm, T_1=298.15 °K, T_2=373.15 °K, n=5 mol V_1-V_5=0.001,1,10,100,1000 m^3				
	L_6, T_1/T_2	L_1, T_1/T_2 V_1	L_2, T_1/T_2 V_2	L_3, T_1/T_2 V_3	L_4, T_1/T_2 V_4	L_5, T_1/T_2 V_5
H_2	2502/2891	499/527	2804/2966	4986/5274	8867/9378	15768/16677
He	1776/2052	354/374	1990/2105	3539/3743	6293/6656	11190/11836
CH_4	887/1025	177/187	994/1051	1768/1869	3143/3324	5589/5912
H_2O	837/967	167/176	938/992	1668/1764	2966/3137	5274/5579
CO	671/776	134/141	752/796	1338/1415	2379/2516	4230/4474
N_2	671/776	134/141	752/796	1338/1415	2379/2516	4230/4474
NO	649/749	129/137	727/769	1292/1367	2298/2431	4087/4323
C_2H_6	648/749	129/137	726/768	1291/1366	2296/2428	4083/4318
O_2	628/726	125/132	704/744	1251/1324	2226/2354	3958/4186
CO_2	536/619	107/113	600/635	1067/1129	1898/2007	3375/3569
C_3H_8	535/618	107/113	600/634	1066/1128	1896/2005	3371/3566
NO_2	524/605	104/110	587/621	1044/1104	1856/1963	3301/3491
C_4H_{10}-n	466/539	93/98	522/552	929/982	1651/1747	2936/3106
Cl_2	422/488	84/89	473/500	841/889	1495/1581	2659/2812
$C_5H_{11}OH$	378/437	75/80	424/448	754/798	1341/1418	2384/2522
C_6H_5OH	366/423	73/77	410/434	730/772	1298/1373	2308/2441
Ratio $\upsilon/\bar{\upsilon}$		0.28/0.27	1.58/1.50	2.82/2.66	5.01/4.74	8.91/8.42



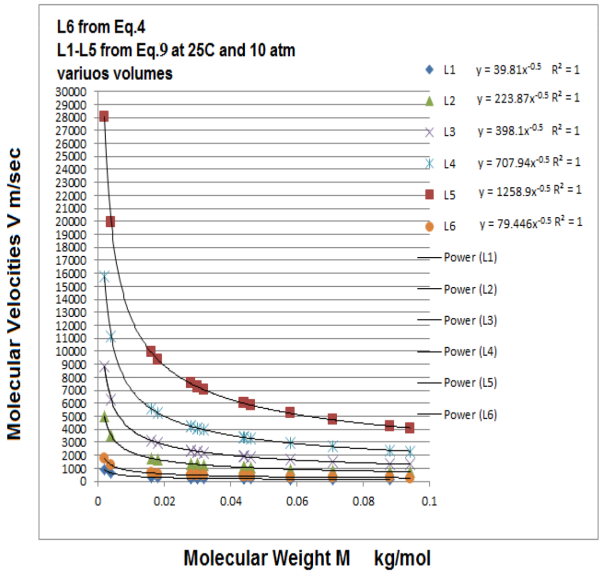


Figure-1: Molecular velocities vs molecular weight for Eq9 &4 at 1atm and 25 °C.

Figure-2: Molecular velocities vs molecular weight for Eq9 &4 at 10 atm and 25 °C.

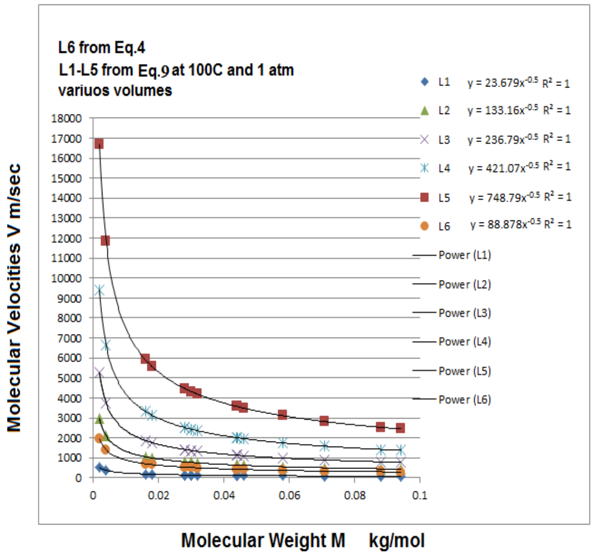


Figure-3: Molecular velocities vs molecular weight for Eq9 &4 at 1atm and 100 °C.

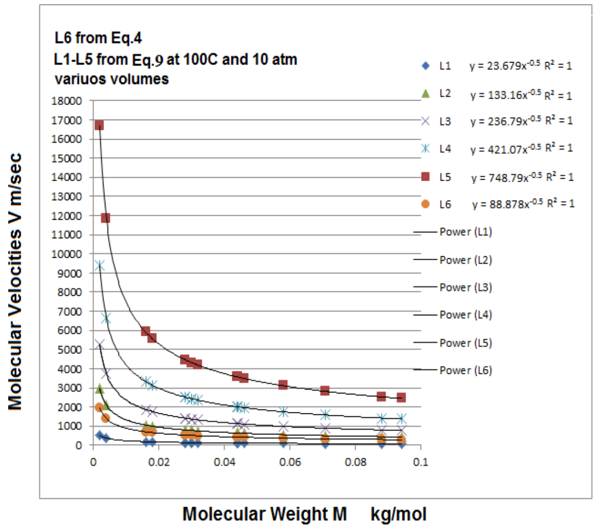


Figure-4: Molecular velocities vs molecular weight for Eq9 &4 at 10 atm and 100 °C.

Second Trial: Tested at several pressures at 10 m^3. The GMV v is also calculated at V=10m^3, pressures (P=10, 20, 40, 60, 80, 100 atm; each pressure is represented by a corresponding line i.e. L_1 and so on), two temperatures (T_1=523.15 °K, T_2=773.15 °K) and $n = 50$ mol as seen in table 3. Figures 5,6 show the effect of these thermodynamic parameters on the GMV v which follow the general power formula $v = B * M^{-0.5}$ m/s; where B value increases with T and P and decreases with concentration (n/V). At L_1 (P_1=2, T_1 and T_2) the B value (B=109) of GMV v converges with the B value (B=105) of KTV $\bar{v}$.

Table 3: The GMV v and KTV $\bar{v}$ values at P=10-100 atm, T=523.15&773.15, n=50, V=10m^3

Materials	Eq.4	Eq.9; V=10m^3, T_1=523.15 °K, T_2=773.15 °K, n=50 mol, P in (atm)					
	T_1/T_2	P_1=10 T_1/T_2	P_2=20 T_1/T_2	P_3=40 T_1/T_2	P_4=60 T_1/T_2	P_5=80 T_1/T_2	P_6=100 T_1/T_2
H_2	2344/2849	3838/4231	4564/5032	5427/5984	6006/6622	6454/7116	6824/7525
He	1663/2022	2724/3003	3239/3571	3852/4247	4263/4700	4580/5050	4843/5340
CH_4	831/1010	1360/1500	1618/1784	1924/2121	2129/2348	2288/2523	2419/2667
H_2O	784 /953	1284/1415	1527/1683	1815/2002	2009/2215	2159/2380	2283/2517
CO	629/764	1030/1135	1224/1350	1456/1605	1611/1777	1731/1909	1831/2019
N_2	629/764	1029/1135	1224/1350	1456/1605	1611/1777	1731/1909	1831/2018
NO	608/739	995/1097	1183/1304	1407/1551	1557/1716	1673/1844	1769/1950
C_2H_6	607/738	994/1096	1182/1303	1405/1549	1555/1715	1671/1843	1767/1948
O_2	588/715	963/1062	1145/1263	1362/1502	1508/1662	1620/1786	1713/1889
CO_2	502/610	821/906	977/1077	1162/1281	1285/1417	1381/1523	1461/1610
C_3H_8	501/609	821/905	976/1076	1160/1279	1284/1416	1380/1522	1459/1609
NO_2	491/596	803/886	955/1053	1136/1253	1257/1386	1351/1490	1429/1575
C_4H_{10}-n	437/531	715/788	850/937	1011/1114	1119/1233	1202/1325	1271/1401
Cl_2	395/480	647/713	770/849	915/1009	1013/1117	1088/1200	1151/1269
$C_5H_{11}OH$	354/431	580/640	690/761	821/905	908/1001	976/1076	1032/1138
C_6H_5OH	343/417	562/619	668/737	794/876	879/969	945/1041	999/1101
Ratio $v/\bar{v}$		1.64/1.48	1.95/1.77	2.32/2.10	2.56/2.32	2.75/2.50	2.91/2.64

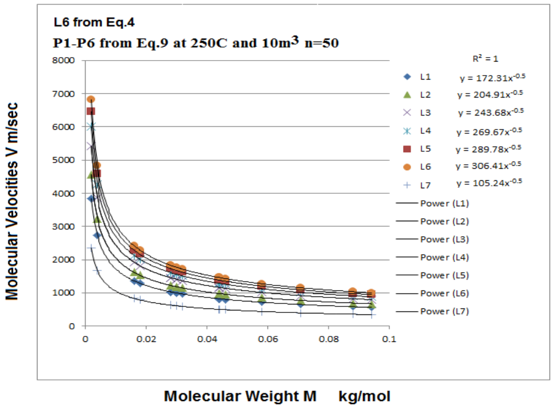


Figure-5: Molecular velocities vs molecular weight for Eq9 &4 at $10m^3$ and 250 °C. (P=10,20,40,60,80,100 atm)

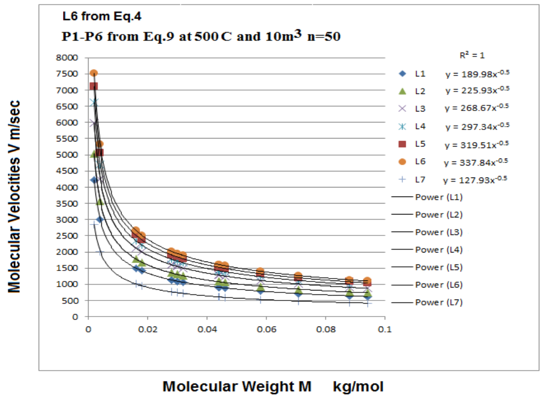


Figure-6: Molecular velocities vs molecular weight for Eq9 &4 at 10 m^3 and 500 °C. (P=10,20,40,60,80,100 atm)

Third Trial: Tested at several pressures at3 $x10^5$ m^3. The GMV $\boldsymbol{v}$ is also calculated at $V=300000m^3$, pressures (P=10, 15, 20, 25, 30, 35 atm), one temperatures (T_1=523.15 °K) and n=5000 mol (c=0.017 mol/m^3). The calculated values of the GMV v followed the general power formula $v = B * M^{-0.5}$ m/s; where B= (717, 794, 853, 902, 944, 980) while the B value of KTV $\bar{v}$ was equal to 105. We may conclude the B values of GMV v become higher than KTV $\bar{v}$ values by a factor 7-9, in comparison with B=105, for concentration of 0.017 mol/m^3 at 523.15 °K as seen in figure 7.

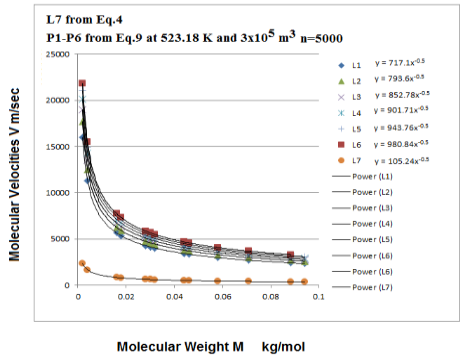


Figure-7: Molecular velocities vs molecular weight for Eq9 &4 at $300000m^3$ and 250 °C. (P=10,15,20,25,30,35 atm)

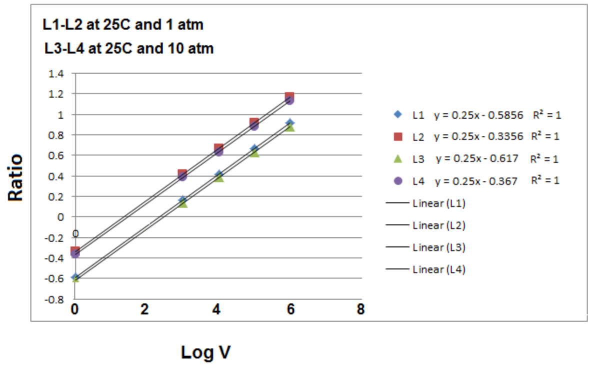


Figure-8: The Ratio of GMV v / KTV $\bar{v}$ versus Log V

The Ratio of GMV $\mathbf{v}$ / KTV $\bar{\mathbf{v}}$: We estimated the **ratio** of $\sum[GMV\ v$ from Equation (9)/ KTV v from Equation (4)] for N materials (N=16), as seen in table1, which is given by the following formula:

$$\textbf{Ratio}=\sum\frac{GMV\ v \text{ from Eq.9}}{KTV\ v\text{from Eq.4}}/N \ \ldots\ldots\ldots\ldots\ldots \text{ At certain } T, P, V, n \qquad (12)$$

Ratio-1 = 0.25x - 0.55, R^2 = 1… at 298.15°K and 1 atm. for V_1-V_5, for N=16, (L_1in Fig.6).
Ratio-2 = 0.25x - 0.30, R^2 = 1… at 298.15°K and 10 atm. for V_1-V_5, for N=16, (L_2in Fig.6).
Ratio-3 = 0.25x - 0.58, R^2 = 1…at 373.15°K and 1 atm. for V_1-V_5, for N=16, (L_3in Fig.6).
Ratio-4 = 0.25x - 0.33, R^2 = 1…at 373.15°K and 10 atm. for V_1-V_5, for N=16, (L_4in Fig.6).

Plotting the average molecular velocities ratio of GMV v / KTV $\bar{v}$ i.e. $(\boldsymbol{v_{E9}}/\boldsymbol{v_{E4}})$ versus the volumes (V_1-V_5, for 16 materials) gives a straight line with correlation coefficient equal to one (R^2=1). Figure-8 shows that the behavior of the molecular velocities ratio follows the pressure effect (P_1=1 atm, P_2=10 atm) rather than temperature effect (T_1=298.15 °K, T_2=373.15 °K). Line No.1, L_1 (P_1=1 atm, T_1=298.15 °K) and Line

No.3, L_3 (P_1=1 atm, T_2=373.15 ^oK) have close intercepts which are higher than the intercepts of L_2 (P_2=10 atm, T_1=298.15 ^oK and L_4 (P_2=10 atm,T_2=373.15 ^oK).

Bimolecular reactions rate constants: A- We calculated the total collision frequency Z_{AB}-GMV v and Z_{AB}-KTV $\bar{v}$ and pre-exponential factors A-KTV and A-GMV from GMV and KTV velocities for the gas phase reaction $H_2 + I_2 \rightarrow 2HI$. The molecular collision diameter d_{12} of I_2 and H_2 value is 4.54 x 10^{-10} m, the reduced mass μ value is 3.321 x 10^{-27} kg and the activation energy is 40361 cal mol^{-1}[17] applying equation (5). We also calculated the rate constants at six temperatures as seen in tables-4,5. Figure 9 showed that the calculated rate constant using GMV v is better than that of KTV $\bar{v}$ using equation no. 6.

Table 4: The rate constants of H_2+I_2 reaction at different temperatures

T ^OK	Z-KTV	Z-GMV	A-KTV	A-GMV	EXP(-E/RT)	RATE-KTV	RATE-GMV	EXP.
584	1.73E+29	4.16E+28	9.46E+11	2.28E+11	1.06986E-16	1.01E-04	2.44E-05	4.45E-05
589	1.76E+29	4.20E+28	9.62E+11	2.30E+11	3.60622E-16	3.47E-04	8.30E-05	1.32E-04
603	1.84E+29	4.29E+28	1.01E+12	2.35E+11	7.6355E-15	7.68E-03	1.80E-03	2.52E-03
611	1.89E+29	4.36E+28	1.04E+12	2.39E+11	4.64648E-14	4.81E-02	1.11E-02	1.41E-02
619	1.94E+29	4.41E+28	1.06E+12	2.42E+11	2.06405E-13	2.19E-01	4.99E-02	6.43E-02
636	2.05E+29	4.53E+28	1.12E+12	2.48E+11	4.26925E-12	4.79E+00	1.06E+00	1.34E+00

Table 5. Logarithmic values of the rate constants of H_2+I_2 reaction

Ln(R-KTV)	Ln(R-GMV)	Ln(R-EXP)	T(^{O}K)	1/T
-9.198793	-10.622617	-10.02002137	584	0.000412
-7.966314	-9.3985384	-8.932708635	589	0.000405
-4.868699	-6.3233637	-5.983496377	603	0.000388
-3.034233	-4.503187	-4.261580482	611	0.000377
-1.51819	-2.9995925	-2.744195648	619	0.000367
1.5659087	0.0571329	0.292669614	636	0.000348

B- We calculated the total collision frequency Z_{AB}-GMV v and Z_{AB}-KTV $\bar{v}$ and pre-exponential factors A-KTV and A-GMV from GMV and KTV velocities for the gas phase reaction $2NOCl \rightarrow 2NO + Cl_2$. The molecular collision diameter d_{12} value is 2.82 x 10^{-10} m, the reduced mass μ value is 5.1036 x 10^{-26} kg and the activation energy is 24387.59 cal/mol[17] applying equation (5). We also calculated the rate constants at seven temperatures as seen in tables-6,7. Figure 10 showed that the calculated rate constant using GMV v is better than that of KTV $\bar{v}$ using equation no. 6.

Table 6: The rate constants of 2NOCl reaction at different temperatures

T(^{O}K)	Z-KTV	Z-GMV	A-KTV	A-GMV	EXP(-E/RT)	RATE-KTV	RATE-GMV	EXP.
298	4.85E+22	1.37E+24	6.82E+10	1.92E+10	1.3226E-18	9.02E-08	2.54E-08	1.19E-08
313	4.51E+22	1.26E+24	6.99E+10	1.94E+10	9.51109E-18	6.64E-07	1.85E-07	8.54E-08
333	4.11E+22	1.13E+24	7.21E+10	1.98E+10	1.00129E-16	7.22E-06	1.98E-06	8.99E-07
353	3.77E+22	1.02E+24	7.42E+10	2.00E+10	8.07315E-16	5.99E-05	1.62E-05	7.25E-06
373	3.47E+22	9.24E+23	7.63E+10	2.03E+10	5.20375E-15	3.97E-04	1.06E-04	4.67E-05
400	3.12E+22	8.17E+23	7.90E+10	2.07E+10	4.79143E-14	3.78E-03	9.91E-04	4.30E-04
420	2.90E+22	7.50E+23	8.09E+10	2.09E+10	2.06409E-13	1.67E-02	4.32E-03	1.85E-03

Table 7. Logarithmic values of the rate constants of 2NOCl reaction

Ln(R-KTV)	Ln(R-GMV)	Ln(R-EXP)	T (^{O}K)	1/T
-16.22169	-17.488246	-18.24884795	298	0.003356
-14.22428	-15.503112	-16.27587647	313	0.003195
-11.83931	-13.133629	-13.92174032	333	0.003003
-9.722895	-11.031791	-11.83436181	353	0.002833
-7.831918	-9.1545919	-9.970830856	373	0.002681
-5.576941	-6.9170861	-7.75066667	400	0.0025
-4.0921	-5.4444427	-6.29013538	420	0.002381

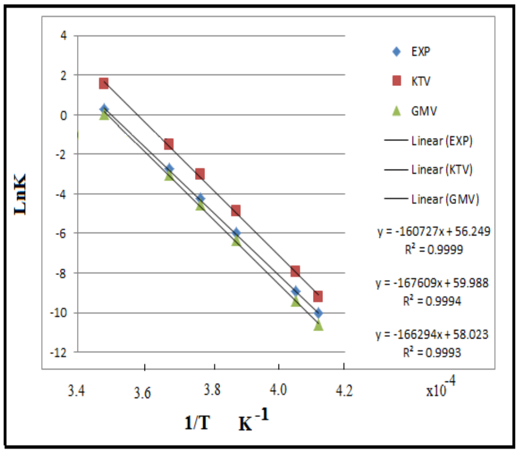


Figure-9: The rate constants of $H_2+I_2 \rightarrow 2HI$ reaction

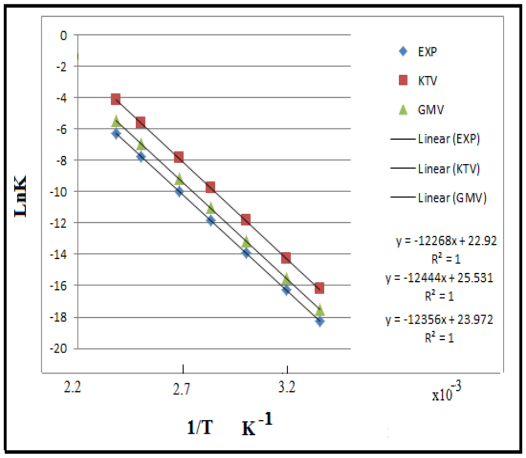


Figure-10: The rate constants of $2NOCL \rightarrow 2NO+Cl_2$ reaction

Other four examples were worked such $CH_3I+(CH_3)_2\text{-}N\text{-}C_6H_5 \rightarrow (CH_3)_3\text{-}N^+(C_6H_5)I^-$, $NO+O_3 \rightarrow NO_2+O_2$, C_2H_4+Butadiene → cyclohexene and $CH_3I+CS(NH_2)_2$ in solution[17]. The results of these reactions also showed that the calculated rate constants using GMV v is better than that of KTV $\bar{v}$ using equation (6) as seen in Figures 11-14.

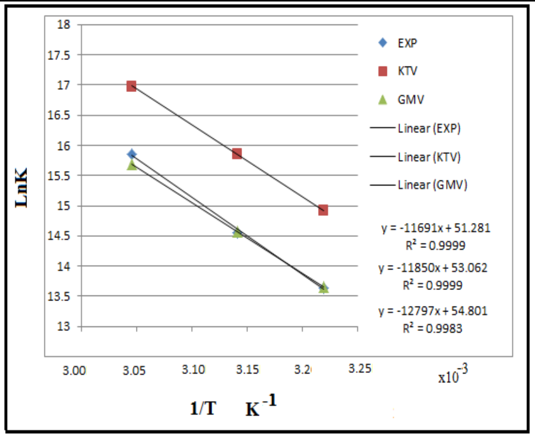


Figure-11: The rate constants of $CH_3I+(CH_3)_2\text{-}N\text{-}C_6H_5 \rightarrow (CH_3)_3\text{-}N^+(C_6H_5)I^-$ reaction

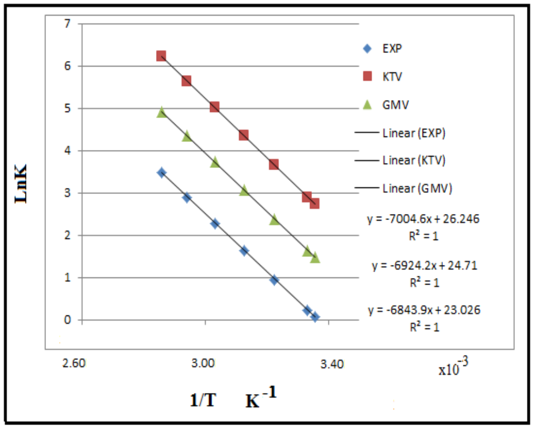


Figure-12: The rate constants of $CH_3I+CS(NH_2)_2$ reaction in solution

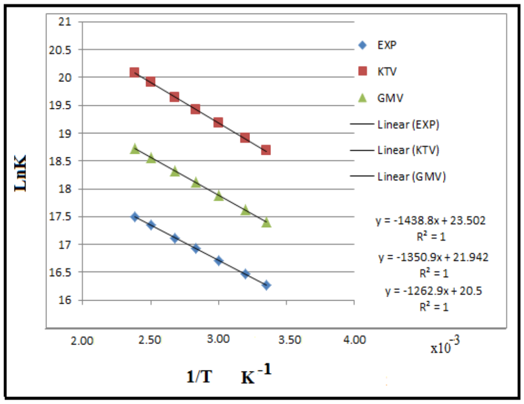


Figure-13: The rate constants of $NO+O_3 \rightarrow NO_2+O_2$ reaction

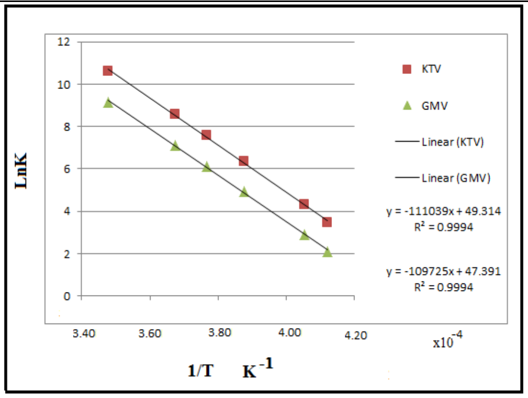


Figure-14: The rate constants of C_2H_4+Butadiene ➔ cyclohexene reaction

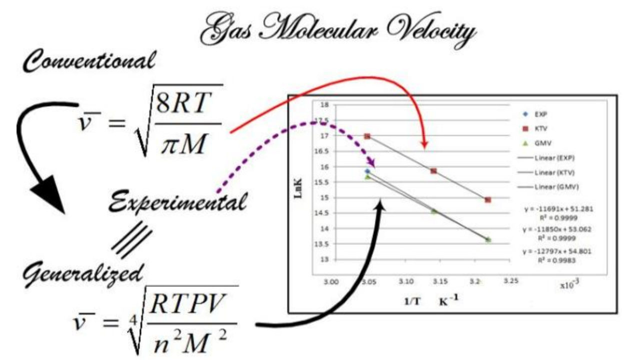


Figure-15: The application of the GMV v in calculating of rate constants gave better fitting with experimental data than that of KTV $\bar{v}$ which revives the collision theory.

CONCLUSIONS

An equation for calculation of a generalized molecular velocity GMV v of the molecule in any reactor has been derived. It includes the thermodynamic parameters T, P, V and n, while the kinetic molecular velocity KTV $\bar{v}$ includes T only. The calculated values of the GMV v in Equation (9) are different from those calculated in KTV $\bar{v}$ of Equation (4) because Equation (9) takes the thermodynamic parameters $(n, T, P$ and $V)$ into consideration. The application of the GMV v in calculating of rate constants of bimolecular reactions gave mcg better fitting with experimental data than that of KTV $\bar{v}$; a fact that revives the collision theory as seen in figure 15.

REFERENCES

[1] R. A. Alberty, "Physical Chemistry" 6th Ed., John Wiley & Sons Books, **1983**, p575-585, ISBN0-471-09284-3.

[2] P. Atkin and J. De Paulo., "Atkin's Physical Chemistry" 8th Ed., W. H. Freeman and Company Books, **2006**, p747-755, ISBN0-7167-8759-8.

[3] R. G. Mortimer, "Physical Chemistry" 3th Ed., Academic Press Books, **2008**, p383-393, ISBN978-0-12-370617-1.

[4] W. J. Moore, "Basic Physical Chemistry", **1986**, Prentice Hall of India, p328- p332.

[5] K. K. Shah and G. Thodos, "Industrial and Engineering Chemistry", 1965, 57(3), 30; L.K.

Athow, 1982, “Real gas considerations for determining physical and thermodynamic properties of gases involved in the prediction of the effects of internal explosions” MSc Thesis; Monterey,California: U.S. Naval Postgraduate School, http://archive.org/stream /realgasconsidera00atho/realgasconsidera00atho_djvu.txt.

[6] S. M. Walas, “Reaction Kinetics for Chemical Engineers”, **1959**, McGraw-Hill, NY, Chap. 11.

[7] G. Soave, “Equilibrium Constants from a Modified Redlich–Kwong Equation of State”, *Chem. Eng. Sci*., **1972**, 27, 1197-1203.

[8] D. Y. Peng and D. B. Robinson, "A New Two-Constant Equation of State". *Ind. Eng. Chem. Fundam.* **1976**, 15, 59–64. doi:10.1021/i160057a011.

[9] R. Stryjek and J. H. Vera, *Can. J. Chem. Eng.* **1986**, 64, 323–333. doi:10.1002/cjce.5450640224.

[10] R. Stryjek and J. H. Vera, *Can. J. Chem. Eng.* **1986,** 64, 820–826. doi:10.1002/cjce.5450640516.

[11] R. Jr. Elliott, S. J. Suresh, and M. D. Donohue, *Ind. Eng. Chem. Res*. 1990, 29 (7), 1476–1485. doi:10.1021/ie00103a057.

[12] J.H. Dymond, and E.B. Smith, “The virial coefficients of pure gases and Mixtures”, **1980**, Oxford University Press.

[13] B. R. Muhyedeen, *European Journal of Scientific Research*, **2008**, 22, 4, October.

[14] B. R. Muhyedeen, *European Journal of Scientific Research*, 2009, 26, 2, Feb.

[15] B. R. Muhyedeen, *European Journal of Scientific Research*, 2013, 100, 1, April.

[16] W. R. Stahl, *Bulletin of Mathematical Biophysics,* **1961,** 23 (4), 355, December.

[17] G. M. Barrow, “Physical Chemistry” 5th Ed., 1983, Tata McGraw-Hill, New Delhi, p747.