

Teaching Techniques and Activities for Gifted

Is there a missed relationship between entropy and kinetic theory of gases? a new perspective for the instruction

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Abstract

This paper is concerned with the investigation for finding missed models that combining between thermodynamic and kinetic theory of gases. The research was initiated by supposing a fixed number of molecules at gas state in a closed box of two equivalents parts. When the barrier between those two parts is removed, the volume of the box will be double of the first stage. It was concluded that the present study gives confirmation for the already existing models with no new developed model unless the employment of Charles's law in derivation process, in spite of the last law is proper for ideal gas rather than the proposed real gas. The derived model of entropy (ΔS) using the last law gives the same value of ΔS that calculated from the standard model. The presented article can be considered as a good exercise for students in order to get an idea of how one could think for connect two different subjects for developing new models which could help in understanding the scientific theories and also in opening new doors of science.

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Introduction

There is no doubt about the significantly importance of thermodynamics and kinetic theory of gases particularly in understanding and predicting the physical and chemical phenomena of systems. Indeed, the thermodynamic parameters including enthalpy, free energy and entropy play an excellent role in most fields of science. On the other side, it is well known that the interesting thermodynamic property of entropy (S) has wide applications in the field of second law of thermodynamics. It is combined with all of the thermodynamical functions such as enthalpy, Gibbs energy, differential equations of Maxwell and Van't Hoff equation (Wu & Guo, 2014; Treumann & Baumjohann, 2019; de Abreu & Vasco Guerra, 2012; Devriendt, 2021; Atkins, 2006). In addition, the second law of thermodynamic was developed by Boltzmann in order to calculate the entropy by statistical approach of probability through the following known equation (Treumann & Baumjohann, 2019; de Abreu & Vasco Guerra, 2012):

$$S = k \ln W$$

where k is the Boltzmann constant and W is the number of energy microstates. In general, the scientists who concerning in this field may realizing the presence of somewhat lack in relationships between thermodynamic and kinetic theory of gases. The aim of the present paper is an attempt deriving new models that combining the entropy and its other related quantities within the framework of classical thermodynamic with the molecular kinetic energy. According to the literature, there is no obvious and direct model expressing the relationship between thermodynamic

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functions with kinetic theory of gases. The present work hopes to provide an idea about the microscopic physical meaning of entropy which could help in understanding the thermodynamic properties.

It should be noted that the kinetic theory of gases was described from thermodynamic point of view by simple classical model. According to this theory, the gas is treated as a composition of numerous submicroscopic particles moving in random motion. It was supposed that the collision of gas particles whether with each other or container is perfectly elastic (ideal gas). Indeed, the last assumption can be considered as a fictional due to presence of molecular interactions or attraction forces between the particles of gas. In other words, the ideal gas does not exist in nature, even the inert gases such as helium atom possesses attraction force of dispersion type with each other (Laidler et al., 2003). Therefore, the suggested relationships by kinetic theory between volume, pressure and temperature are only limited to ideal gas. However, the modification of ideal gas law by van der Waals concerning the molecular interactions between gas particles in addition to their molecular size was done with a remarkable complexity.

Aim of Instructional Activity

In order to find a new relationship that could combine the topic of thermodynamic with that of kinetic theory of gases. The yield of this investigation is very interesting for understanding these scientific disciplines as well as can be considered as optimum exercise for young scientists.

Instruction of the Entropy and Gas Theory

Well, considerable efforts must be paid for deriving or building up any scientific model. Since the equation is a mathematical relationship, the process of obtaining it is not easy or direct and falls within trial and error. Therefore, the derivation process requires a high degree of patience. For example, Schrödinger took a period of two years to derive his famous equation in quantum mechanics (Khalil, 2020). Thus, according to second law of thermodynamic, the entropy can be defined as a measure of the distribution of energy in the system (Atkins, 2006; Yee & Sjögreen, 2020; Laidler et al., 2003; Callen, 1985; Daniels & Alberty, 1979). Such a distribution of the system increases with increasing the temperature and vice versa unless reaching the temperature of absolute zero (Atkins, 2006). On the other side, one could understand from the laws of gases that the kinetic energy of gases has a direct proportional with the temperature, due to the increasing in the kinetic energy of molecules. According to the law of the kinetic theory of gases, one could find the following relationship (Atkins, 2006):

$$PV = \frac{1}{3} Nmv^2 \quad (1)$$

where P is the pressure, V is the volume, N is the number of molecules, m is the molecular mass of the gas and v it is the velocity. Multiply equation 1 by $3/2$ one could get:

$$\frac{3}{2} PV = \frac{1}{2} Nmv^2 \quad (2)$$

The kinetic energy (K_E) is equal to $1/2mv^2$ which can be substituted in equation 2 in order to give:

$$\frac{3}{2} PV = NK_E \quad (3)$$

In the case of real gases, the general law according to Virial equation of gases which is derived from perturbative treatment of statistical mechanics could be represented by the following equation (Devriendt, 2021; Atkins, 2006; Callen, 1985):

$$PV_m = RT \left[1 + \frac{A(T)}{V_m} + \frac{B(T)}{V_m^2} + \frac{C(T)}{V_m^3} + \dots \right] \quad (4)$$

where V_m is the molar volume, R is the ideal gas constant, T is the absolute or Kelvin temperature, A , B , and C are temperature dependent constants. The term between the brackets of the above equation (4) can be abbreviated by ω symbol as following:

$$PV_m = RT\omega \quad (5)$$

By combination equation 5 with that of 3 for one mole of gas one could obtain the following relationship:

$$K_E = \frac{3}{2} RT\omega \quad (6)$$

Now, if one suppose there is an isothermal system of a fixed dimensional box containing M number of real gas molecules. This box is divided into two equivalents parts by a suitable barrier as illustrated in Figure 1. Therefore, the kinetic energy of these molecules (K_{E1}) can be expressed by equation 7 as the sum of the kinetic energies of molecules. When the barrier is removed the molecules will diffuse to the other part of the system as the new volume (V_2) is the double of V_1 ($V_2=2V_1$), and the kinetic energy of this new system (Figure 2) will be termed as K_{E2} .

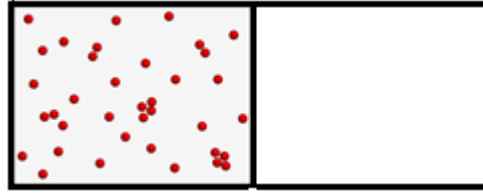


Figure 1. Virtual box of fixed dimensions including a barrier

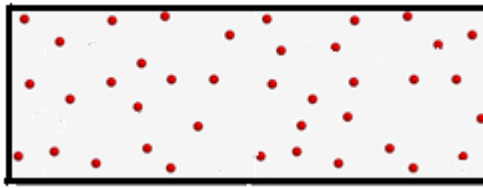


Figure 2. Virtual box of fixed dimensions without the barrier

The total kinetic energy of M molecules can be expressed as the sum of the kinetic energies of all molecules ($K_E = \sum_{i=1}^M \frac{1}{2}mv^2$). Since the proposed system contains identical molecules, the averaged kinetic energy of these molecules are also identical. Thus, the total energy of the system may be expressed by the following equation:

$$K_E = \left(\frac{1}{2}mv^2\right) M \quad (7)$$

where $\frac{1}{2}mv^2$ is the averaged kinetic energy, M is the number of molecules at the system. The total kinetic energy of V_1 (Figure 1) and V_2 (Figure 2)) can be expressed as K_{E1} and K_{E2} respectively (equations 8 and 9).

$$K_{E1} = \left(\frac{1}{2}mv_1^2\right) M \quad (8)$$

$$K_{E2} = \left(\frac{1}{2}mv_2^2\right) M \quad (9)$$

where v_1 and v_2 are the averaged molecular velocities of the gas molecules at V_1 and V_2 , respectively. The molecular linear momentum (p) is equal to mv which can be substituted in equations 8 and 9 (multiplying the right side by m/m) to give equations 10 and 11, respectively.

$$K_{E1} = \left(\frac{p_1^2}{2m}\right) M \quad (10)$$

$$K_{E2} = \left(\frac{p_2^2}{2m}\right) M \quad (11)$$

Dividing eq. 10 by that of 11 one could get:

$$\frac{K_{E1}}{K_{E2}} = \frac{\left(\frac{p_1^2}{2m}\right) M}{\left(\frac{p_2^2}{2m}\right) M} \quad (12)$$

which then gives

$$\frac{K_{E1}}{K_{E2}} = \frac{p_1^2}{p_2^2} \quad (13)$$

It is clear that the volume at the second state becomes the double of the first state which can be expressed as following:

$$V_2 = 2V_1 \quad (14)$$

or

$$\frac{V_1}{V_2} = \frac{1}{2} \quad (15)$$

At this case, if one suppose that the Charles's law of isobaric system can be applied to the suggested isothermal system (the temperature has direct proportionality with the volume) using the following relation (Daniels & Alberty, 1979). This may be somewhat attributed to that of Charles's law is suitable to ideal gas rather than the postulated real gas as the energies of attraction and repulsion between molecules are affected directly by the expansion process in comparison to that of ideal gas.

$$T \propto V$$

then

$$T = \varphi V \quad (16)$$

where φ is the constant term.

By substitution eq. 16 into that of 6 for one mole of V_1 and V_2 one could get the following:

$$K_{E1} = \frac{3}{2} R \varphi V_1 \omega \quad (17)$$

$$K_{E2} = \frac{3}{2} R \varphi V_2 \omega \quad (18)$$

Substitution eqs. 17 and 18 into that of eq. 13 one could get the following:

$$\frac{\frac{3}{2} R \varphi V_1 \omega}{\frac{3}{2} R \varphi V_2 \omega} = \frac{p_1^2}{p_2^2} \quad (19)$$

$$\frac{V_1}{V_2} = \frac{p_1^2}{p_2^2} \quad (20)$$

$$\frac{p_1^2}{p_2^2} = \frac{1}{2} \quad (21)$$

Thus $p_2^2 = 2p_1^2$

Then, substituting eq. 13 into that of eq. 21 one could obtain:

$$\frac{K_{E1}}{K_{E2}} = \frac{1}{2} \quad (22)$$

Hence, one could realize clearly that the kinetic energy of Figure 2 (K_{E2}) is twice that of Figure 1 (K_{E1}). Since equations 15 and 22 are both equal to same quantity of $1/2$. Therefore,

$$\frac{K_{E1}}{K_{E2}} = \frac{V_1}{V_2} \quad (23)$$

Interestingly, this means that the kinetic energy has a direct proportional with the volume, and it is clear that the ratio between the first volume and second volume is equal to $1/2$, as following:

$$K_{E2} = 2K_{E1} \quad (24)$$

Equations 23 and 24 can be represented in terms of velocity ($K_E = \frac{1}{2} m v^2$) in order to give equations 25 and 26 respectively as following:

$$\frac{v_1}{v_2} = \frac{V_1}{V_2} \quad (25)$$

$$v_2 = 2v_1 \quad (26)$$

The above equations (23-26) indicate that the potential energy of gas molecules are changed to that of kinetic energy when the volume of expanded and vice versa. In other words, these relationships are contradict with that of non-

changing in kinetic energy due to isothermal expansion for ideal gasses. However, it is may be true for the real gas as proposed hypothetically at this work. Indeed, the most useful form of the second law for physicochemical applications is expressed in terms of an additional thermodynamic function of entropy (S). It is a function of the state of system and has the following properties. For an infinitesimal reversible process: $= \frac{\partial q}{T}$, and for an infinitesimal spontaneous process: $dS > \frac{\partial q}{T}$, where q is the heat and T is the absolute temperature. On the other hand, for isothermal process the entropy can be given by the following equation (Atkins, 2006; Daniels & Alberty, 1979):

$$\Delta S = R \ln \frac{V_2}{V_1} \quad (27)$$

Dividing both sides of equation 27 by R gives:

$$\frac{\Delta S}{R} = \ln \frac{V_2}{V_1} \quad (28)$$

The reciprocal of equation 23 is:

$$\frac{K_{E2}}{K_{E1}} = \frac{V_2}{V_1} \quad (29)$$

By taking the natural logarithm (\ln) of both sides of equation 29 one could get:

$$\ln \frac{K_{E2}}{K_{E1}} = \ln \frac{V_2}{V_1} \quad (30)$$

Hence, the right sides of both equations 28 and 30 are equal, therefore, their left sides are equal too which can be expressed by the following relation:

$$\frac{\Delta S}{R} = \ln \frac{K_{E2}}{K_{E1}} \quad (31)$$

Multiplying both sides of equation 31 by R one could get the following important relationship:

$$\Delta S = R \ln \frac{K_{E2}}{K_{E1}} \quad (32)$$

The last model might also be expressed by the term of the velocity terms in a similar manner to that of equation 25 as following:

$$\Delta S = R \ln \frac{v_2}{v_1} \quad (33)$$

Thus, the last two equations are representing the endeavor of the present assumption as they combining they between thermodynamic and the kinetic theory of gases. However, it is not true to use Charles's law in this study which could only applied for isobaric systems (Daniels & Alberty, 1979). But, at the same time, as mentioned above, the last law is for ideal gases, not for real gases. On the other side, the Boyle's law ($P \propto \frac{1}{V}$) is more suitable for the present study which therefore no new model could be derived from the present work. In other words, equation 20 can be represented by the following form:

$$\frac{P_1 V_1}{P_2 V_2} = \frac{p_1^2}{p_2^2} \quad (34)$$

According to Boyle's law:

$$P_1 V_1 = P_2 V_2$$

Then equation 34 can be represented as following:

$$\frac{p_1^2}{p_2^2} = 1$$

which means no change in the average of kinetic energy due to change from V_1 to V_2 ($K_{E1} = K_{E2}$) and the value ΔS can be determined using equation 27 will give the same value of equations 32 and 33.

Conclusions

On the bases of the achieved results, one could conclude that there is no acceptable success in reaching the endeavor of the present work by suggesting developed relationships between the thermodynamic and the kinetic theory of gases. In other words, no new scientifically acceptable models are achieved for combining between the thermodynamic and the kinetic theory of gases except if one employ Charles's law in the derivation process. However, the last law should not be applied to the proposed system as an isothermal, but at the same time, the proposed gas is a real which not obey completely on Charles's law in contrast the perfect gas. This because the real gases are suffering from electrostatic interactions which may affected by expansions and contractions even at isothermal process. The new developed model using Charles's law of entropy (equations 32 and 33) yield the same value of that of standard model (equation 27). Thus, the presented article could give an example for students about how one supposes something hypothetically in order to find new relationship. Of course, such new derived relationship if can be verified would be quite helpful for understanding the physical meanings of any selected topic.

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