

Lecture Note

Geometrical Representation of Gas Properties
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Abstract

The perfect gas equation, laws, principles and processes as well as the van der Waals equation for real gases are represented geometrically. Intensive and extensive properties and the standard temperature and pressure (STP) condition are shown too. Plane geometry offers a supplementary method to the piston formulation for explaining and visualizing gas properties. Several difficulties and misconceptions of students may thus be resolved.

Keywords: Gas, Geometrical, van der Waals.

1. Introduction

It is a common practice in almost every standard physical chemistry textbook [1-2] the properties of gases to be at the very beginning. This is pedagogically highly recommended because it introduces students, in a comprehensive way, to both the history and the major concepts of thermodynamics. The usual content includes: a) the perfect gas laws and from them how the perfect gas equation is constructed and b) the behavior of the real gases and how they deviate from the ideal situation; mainly explained with the aim of the van der Waals equation [3-4]. At the same time several definitions on extensive and intensive properties are given and several processes are described.

A cylinder with a piston enclosing the working gas under consideration is the main instrument for the visualization of all these concepts, processes and definitions [5-6]. Although the piston is a great paradigm, there are a few more things that may be better understood if this instrument is supplemented by another one of a completely different nature. To this end, a geometrical description for both real and ideal gas behavior is drawn here.

As a matter of fact, the use of geometry for explaining various physical chemistry processes has already been demonstrated. Levin has suggested that the phase rule and Euler's equation are synonymous and again the phase diagram can be treated topologically [7]. Nash has deployed plane geometry to discuss the Carnot cycle and Maxwell's relations in order to overtake partial differentials [8]. He stressed out that '*this is the way Maxwell himself derived these equations*' in his theory of heat [9]. Notable to this direction are Gibbs diagrams for the perfect gas and a method for geometrical representation of the thermodynamic properties [10].

In this article it will be shown how intensive and extensive properties can be defined geometrically and again how the perfect gas equation together with all relevant laws, principles and processes as well as the real gas equation of state can be derived from plane geometry. Several hidden

details and several students' misconceptions may thus be clarified.

2. The Perfect Gas

First, let us consider an angle defined by the interception of two semi-lines (Fig. 1a). Although OX and OY can extend to infinity the angle θ does not change; that is, the semi-lines are extensive properties of the system whereas the angle is an intensive one. Second, a line segment h normal to OX is also dependant from its location on OX (i.e. it is also an extensive property). However, by dividing it with its abscissa distance from the origin the resulting quantity turns to be an intensive one ($h/q=h'/q'=const.$).

Next, let us draw an arbitrary line kx to define an obtuse triangle Okx. The area of this triangle is $A=1/2xh=1/2xksin\theta$. By rearranging this equation and changing the nomenclature results to:

$$\left[\frac{h}{x} \right]_P \cdot x = k \cdot \left[\frac{1}{2} \right]_R \cdot \sin \theta \Rightarrow PV = nRT \quad (1)$$

Eq. (1) is a geometrical representation of the perfect gas equation, with two extensive ($x=V/volume$ and $k=n/moles$) and two intensive properties ($h/x=P/pressure$ and $\sin\theta=T/temperature$). When a molar version is more convenient, a geometrical representation may be constructed by setting $Ok=1$ to be the radius of a circle (O, k).

By drawing $k'x'$ parallel to kx, $k/k'=x/x'$ (see Fig. 1b), Eq. (1) takes on the form:

$$x \cdot k' = x' \cdot k = const. \Rightarrow \frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (2)$$

Eq. (2) is the Avogadro's principle.

In Fig. 1c the isothermal process is shown. By keeping θ , h and k constant and by extending (or shortening) x to x', Eq. (1) takes on the form:

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$$\left[\frac{h}{x} \right]_{P_1} \cdot x = \left[\frac{h}{x'} \right]_{P_2} \cdot x' = const. \Rightarrow PV_1 = P_2V_2 \quad (3)$$

Eq. (3) is a geometrical representation of Boyle's law.

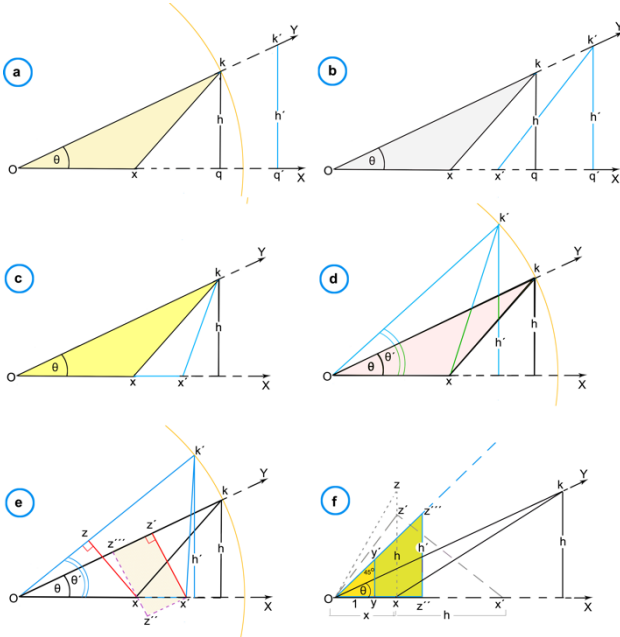


Fig. 1. Geometrical representation of perfect gas properties: a) equation of state; b) Avogadro's principle; c) Boyle's law; d) Gay Lussac law; e) Charles' law; f) STP condition

In Fig. 1d the isochoric process is shown. By keeping x constant and by moving radius k to a different position on the perimeter of the circle ($k=k'$), Eq. (1) takes on the form:

$$\left[\frac{h}{x} \right]_{P_1} \cdot \sin \theta' = \left[\frac{h'}{x} \right]_{P_2} \cdot \sin \theta = const. \Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (4)$$

Eq. (4) is a geometrical representation of Gay Lussac's law.

In Fig. 1e an isobaric process construction is depicted. Triangles Okx and $Ok'x'$ are the required result because $h/x = h'/x'$. Notice that $h = k \sin \theta$ and $h' = k' \sin \theta'$ (where $k=k'$). In order $x' \sin \theta'$ to be equal to $x \sin \theta$, xz must be equal to $x'z'$. Then $z'z''$ is constructed normal to Ok and equal to xz and $z''x'$ parallel to Ok ; point x' is now defined and Eq. (1) takes on the form:

$$x \cdot \sin \theta' = x' \cdot \sin \theta = const. \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (5)$$

Eq. (5) is a geometrical representation of Charles' law.

In Fig. 1f the STP condition is shown. The arbitrary triangle Okx has an area equal to triangle Oxz ($xz=h$). Then an auxiliary right triangle $Oz'x'$ with height $(xz')^2 = xh$ is constructed. After that, a right isosceles triangle $Oz''z'''$ with $Oz'' = z''z''' = xz'$ and area equal to the original one, $A(Okx) = A(Oz''z''')$, is constructed too. By normalizing $Oz''z'''$ sides to $Oy = Oy' = 1$, the STP triangle Oyy' is obtained. Since Oyy' is similar to $Oz''z'''$ there must be a similarity factor Q such that:

$$\frac{A(Okx)}{Q} = A(Oyy') = 1 \Rightarrow \frac{PV}{nRT} = \frac{P^o V_m}{RT^o} = 1$$

$$= \frac{10^5 Pa \times 22.7 \times 10^{-3} m^3}{1 mol \times 8.314 \frac{J}{mol \cdot K} \times 273.15 K} = 1 \quad (6)$$

Eq. (6) is a geometrical representation for the STP condition.

3. Real Gases

Real gases deviate from the ideal behavior and pedagogically the best equation to describe this deviation is the van der Waals equation. The pressure for the real gas is corrected by a factor a/V^2 and the volume by a factor b ; where a and b are the van der Waals coefficients.

In Fig. 2 the geometrical representation of the van der Waals equation ($Ok'x'$) is illustrated together with the perfect gas equation (Okx). The volume of the ideal gas $x > x'$ ($x - x' = b$) and the pressure $h/x > h'/x'$. The area of triangle $Ok'x'$ (real gas) is equal to $x'h' = k' \sin \theta'$ and that of Okx (ideal gas) is $xh = k \sin \theta$. By correcting the deviations, Eq. (1) takes on the form:

$$(x - b) \frac{h'}{x - b} = k' \sin \theta' \quad (7)$$

With the aid of Taylor series Eq. (7) becomes:

$$(x - b) h' \left(1 + \frac{b}{x} \right) = k' x \sin \theta' \quad (8)$$

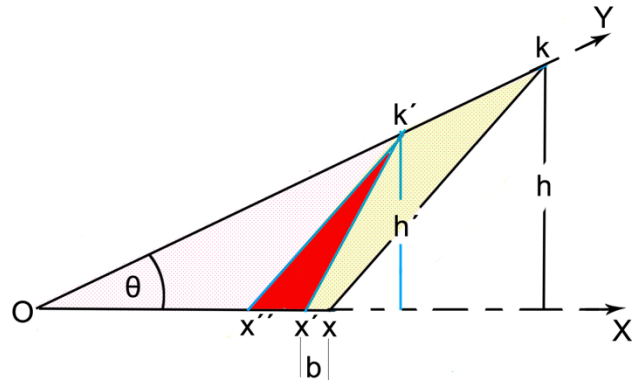


Fig. 2. The van der Waals equation.

From the similar triangles Okx and $Ok'x''$ it comes that $k'x = kx''$. Since $x' > x''$ there will be a factor $c' > 1$ such that $x'/c' = x''$ and thus $k'x = kx'/c'$. Substituting to Eq. (8):

$$(x - b) \frac{h'}{x'} \left(c' + \frac{bc'}{x} \right) = k \sin \theta \quad (9)$$

By replacing c' with a c such that $c' + bc'/x = 1 + bc/x$ and by introducing a constant $a = h'bcx/x'$, Eq. (9) with $k=1$ becomes:

$$\left(\frac{h'}{x'} + \frac{a}{x'^2} \right) \cdot \left(\frac{x - b}{V_i} \right) = k \sin \theta \Rightarrow \left(P_R + \frac{a}{V_i^2} \right) \cdot (V_i - b) = RT \quad (10)$$

Where the subscripts R=real and I=ideal; Eq. (10) is the customary van der Waals equation for 1 mol.

4. Conclusions

The outlined geometrical representation of gas properties is based on a simple fact. The area of a triangle can be obtained from a Euclid calculation as well as from a trigonometric measure. In the first case the base of the triangle and its height are involved whereas in the second case the height is substituted by the sine of the formed angle. Landsberg has also defined the perfect gas by two equations: $pV=gU$ (where g is a constant and U the internal energy) for the *ideal gas* and by the additional relation $pV=Nk_B T$ (where N is the number of particles and k_B the Boltzmann constant) for the *ideal classical gas* [11].

From Fig. 1a it is easy to visualize the realm of intensive and extensive properties [12]. Sine of angle θ is an intensive property (e.g. like temperature defined by the zero law of thermodynamics [13]) because it is a ratio of two extensive properties, $\sin\theta=h/k$. Again h/q is an intensive property because it is also the ratio of two extensive properties (e.g. like pressure, defined as a fraction of force over area). Since $k/k'=q/q'$, q/k is in general an intensive property; as all molar quantities being.

The energy of the system is related to the height of the triangle. From equation $x(h/x)=k\sin\theta$ it is concluded, for $k=1$, that $h=\sin\theta$. The internal energy of the system depends only from the temperature; as it is expected for the perfect gas. During an isothermal process h remains unchanged; i.e. $\Delta U=0$ (see Fig. 1c).

In Fig. 1f the STP condition is represented by an isosceles right triangle of unit side. The geometrical construction is based on equal areas. This is a legitimate modification of the original triangle and this is the kernel of the idea to have an STP condition. Algebraically a situation at a given P, V, n, T state can reduce to a standard condition P^0, V_m, T^0 because both ratios are equal to 1. In this study the STP triangle is similar to an intermediate triangle (there will always be such a triangle) having an area equal to the original one.

For real gases the derivation of the van der Waals equation reveals that the constant $\alpha=h'bx/x'$ depends from the energy of the real gas times the excluded volume times the ratio of ideal to real volumes; but not from the temperature. Therefore, it is not a universal constant; it is limited to a given gas. The equation for 1 mol is commonly presented as:

$$\left(P + \frac{a}{V^2}\right) \cdot (V - b) = RT \quad (11)$$

However Eq. (11) is a source of confusion. To what real or ideal quantity each parameter refers. If $P_R < P_I$ and $V_R < V_I$ the expected correction it would be:

$$\left. \begin{array}{l} P_R + \frac{a}{V^2} = P_I \\ V_R + b = V_I \end{array} \right\} \Rightarrow \left(P_R + \frac{a}{V^2}\right) \cdot (V_R + b) = P_I V_I = RT \quad (12)$$

Apparently, Eq. (12) is not the equation which van der Waals proposed; there is a twist on the constants which usually is omitted from textbooks. The given geometrical representation resolves this puzzle with Eq. (10) in a much easier way than other approaches [14-16].

Pedagogically, Euclid geometry is the best instrument to describe, if possible, physical phenomena. The reason is that plane geometry is cognitively more perceptive than other methods; especially when connotations are involved.

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