

EQUATION OF STATE IN FORM WHICH RELATES MOL FRACTION AND MOLARITY OF TWO (OR MORE) COMPONENT THERMODYNAMIC SYSTEM CONSISTED OF IDEAL GASES, AND IT'S APPLICATIONS

by

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Most people would face a problem if there is a need to calculate the mole fraction of a substance A in a gaseous solution (a thermodynamic system containing two or more ideal gases) knowing its molarity at a given temperature and pressure. For most it would take a lot of time and calculations to find the answer, especially because the quantities of other substances in the system are not given. An even greater problem arises when we try to understand how special relativity affects gaseous systems, especially solutions and systems in equilibrium. In this paper formulas are suggested that greatly shorten the process of conversion from molarity to mole fraction and give us a better insight into the relativistic effects on a gaseous system.

Key words: *mol fraction, molarity, ideal gas, equation of state, special relativity*

Introduction

Most people including specialists believe that a model was made that absolutely describes the thermodynamic system consisted of an ideal gas. Indeed the ideal gas state equation connects well all the parameters in an ideal gas system. But if we try to solve the following problem: a thermodynamic system consists of two ideal gases A and B which are contained in some volume V (not given) at a given temperature T , and at given total pressure P . The molarity of gas A is given. Find the mole fraction of ideal gas A!

In its basic form the ideal gas state equation can not help us solve this problem, simply because it does not include mole fraction. Most people including specialists would say this is impossible, and would require additional data, for example, volume. But is additional data really necessary, or can the solution be found more easily even without them?

Theoretical analysis

Let us consider. In case the chemical system consists of two monoatomic ideal gases A and B then the state of the system is given as:

$$PV = (n_A + n_B)RT \quad (1)$$

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where V is the total volume of the system, P its total pressure which equals the sum of partial pressures of gases in it, n_A is the quantity of ideal gas A, and n_B – the quantity of ideal gas B.

As the definition of the molarity is:

$$[A] = \frac{n_A}{V} \quad (2)$$

by combining expressions (1) and (2) we have:

$$[A] = \frac{n_A P}{(n_A + n_B)RT} \quad (3)$$

where $\chi_A = n_A/(n_A + n_B)$ is the mole fraction of the substance A. Therefore:

$$[A] = \chi_A \frac{P}{RT} \quad (4)$$

or

$$\chi_A = [A] \frac{RT}{P} \quad (5)$$

This expression presents the relations between two ways of expressing the concentration in chemistry.

By replacing $[A]$ from expression (2) to relation (5) we obtain:

$$\chi_A = \frac{n_A RT}{PV} \quad (6)$$

The use of eqs. (4), (5), and (6) to solve the problem given in the introduction will be discussed later, as well as its application in relativistic thermodynamics.

Applications

Using eq. (5) the problem above which seemed unsolvable becomes a piece of cake. All we need to know to calculate the mole fraction in a given system is its temperature, total pressure, and molarity of the substance for which we are calculating mole fraction. Note that since no parameters for other substances in the system are required for eqs. (4) and (5) we can easily transform from one type of concentration to another without even knowing about the presence of other substances in the system.

As we saw in the introduction some problems can not be solved without eqs. (5) and (6). On the other hand there are some problems that can be solved without eqs. (5) and (6), but that require extensive calculations, and a lot of time.

For example to find the equilibrium constants K_p and K_c for the reaction $N_2O_4 \rightleftharpoons 2NO_2$, if it is known that 20% of initial quantity (mols) of N_2O_4 has dissociated at a temperature of 300 K, before the system reached equilibrium (the total pressure of the equilibrium mixture is 101.3 kPa). Solving this problem becomes much easier, shorter and faster if we do use eqs. (5) and (6).

The eqs. (5) and (6) can be used to analyze the effects of special relativity on a thermodynamic system. A thermodynamic system consisted of two ideal gasses A and B is in relativistic movement. According to special theory of relativity the relativistic contraction of space occurs:

$$X = X_0 \sqrt{1 - \frac{v^2}{c^2}} \quad (7)$$

where X' is the length of the system in relativistic movement, v – the velocity of the system, and c – the speed of light. The consequence of relation (7) is, according to [1], relativistic volume:

$$V = V_0 \sqrt{1 - \frac{v^2}{c^2}} \quad (8)$$

and according to [2] relativistic molar concentration:

$$[A] = \frac{[A]_0}{\sqrt{1 - \frac{v^2}{c^2}}} \quad (9)$$

Now we can analyze the relativistic effects on a system using eqs. (5) and (6).

The thermodynamic system given above is now in relativistic movement. The observer 1 rests, while the observer 2 is in the system, moving with it. The observer 2 doesn't notice any changes in the system. The observer 1 notices according to expressions (7), (8), and (9) relativistic space contraction, volume, and molarity. By applying eq. (5) to a system in relativistic movement we obtain according to [3]:

$$\chi = [A] \frac{RT}{P} \quad (10)$$

The mole fraction according to conservation law is not affected by relativity, so:

$$\chi = \chi' \quad (11)$$

Now we substitute eq. (5) and (10) to (11):

$$\frac{[A]RT}{P} = \frac{[A]'RT'}{P'} \quad (12)$$

1907 Planck demonstrated that pressure is Lorentz invariant [4]. If $P' = P$ eq. (12) becomes:

$$[A]RT = [A]'RT' \quad (13)$$

where according to Ohsumi [2] $[A]' = [A]/[1 - (v^2/c^2)]^{1/2}$,

Landsberg [5, 6], and others [3, 7, 9-12] stated that temperature should be Lorentz invariant, so $T = T'$:

In that case, from eq. (13) we can conclude that R must be Lorentz co-variant.

$$R = R_0 \sqrt{1 - \frac{v^2}{c^2}} \quad (14)$$

This allow us to conclude that the Boltzmann constant is Lorentz co-variant too:

$$k_B = k_{B0} \sqrt{1 - \frac{v^2}{c^2}} \quad (15)$$

which is in agreement with the conclusions of Avramov [7]. This statement presents a problem for statistical thermodynamics, since it implies that the entropy must be co-variant as well.

However, entropy is a state function and can not be Lorentz co-variant. The Planck's theorem of entropy invariance [4], as well as Ott [8], and many other authors such as Bormashenko [9] and Popović [10] confirm the entropy invariance.

Entropy is given as:

$$S = k_B \ln W \quad (16)$$

is the Boltzman constant, where W is the probability given as:

$$W = (CV)^N \quad (17)$$

In relativistic conditions the equation above becomes:

$$W' = (C'V')^N$$

$$N \quad N \quad C \quad C \quad V \quad V \sqrt{1 - \frac{v^2}{c^2}}$$

Let us back to the eq. (15). k_B is Lorentz invariant claim Bormashenko [11] in opposite to eq. (15). Now, if $S = S'$, and $k_B = k'_B$, then: $W = W'$. In that case there are no difference between eqs. (16) and (18):

$$S' = k'_B \ln W' \quad (18)$$

Solution is to take effective volume in calculation [12]. It means that one liter is still one liter in relativistic condition even with different nominal value:

$$V'_{\text{ef}} = V_{\text{ef}} \quad V_{\text{ef}} = V$$

$$V_{\text{ef}} \quad V \quad \frac{V}{\sqrt{1 - \frac{v^2}{c^2}}}$$

where V is the volume at rest, V' – the relativistic volume, V_{ef} – the effective volume, and V'_{ef} – the relativistic effective volume. Effective volume does not depend on speed of the inertial system, so in such a way it is possible for relativistic space contraction to be real and for thermodynamic parameters to be Lorentz invariant.

Conclusions

For a solution containing ideal gasses A and B the relation of their mole fraction and molarity is given by eqs. $\chi_A = [A](RT/P)$ and $\chi_A = n_A RT/PV$.

This relation is applicable to any thermodynamic system containing two or more ideal gasses. These relations can also be used in relativistic thermodynamics.

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