

Gas laws for transformer dissolved gas analysis

DGA starting from the ideal gas equation of state

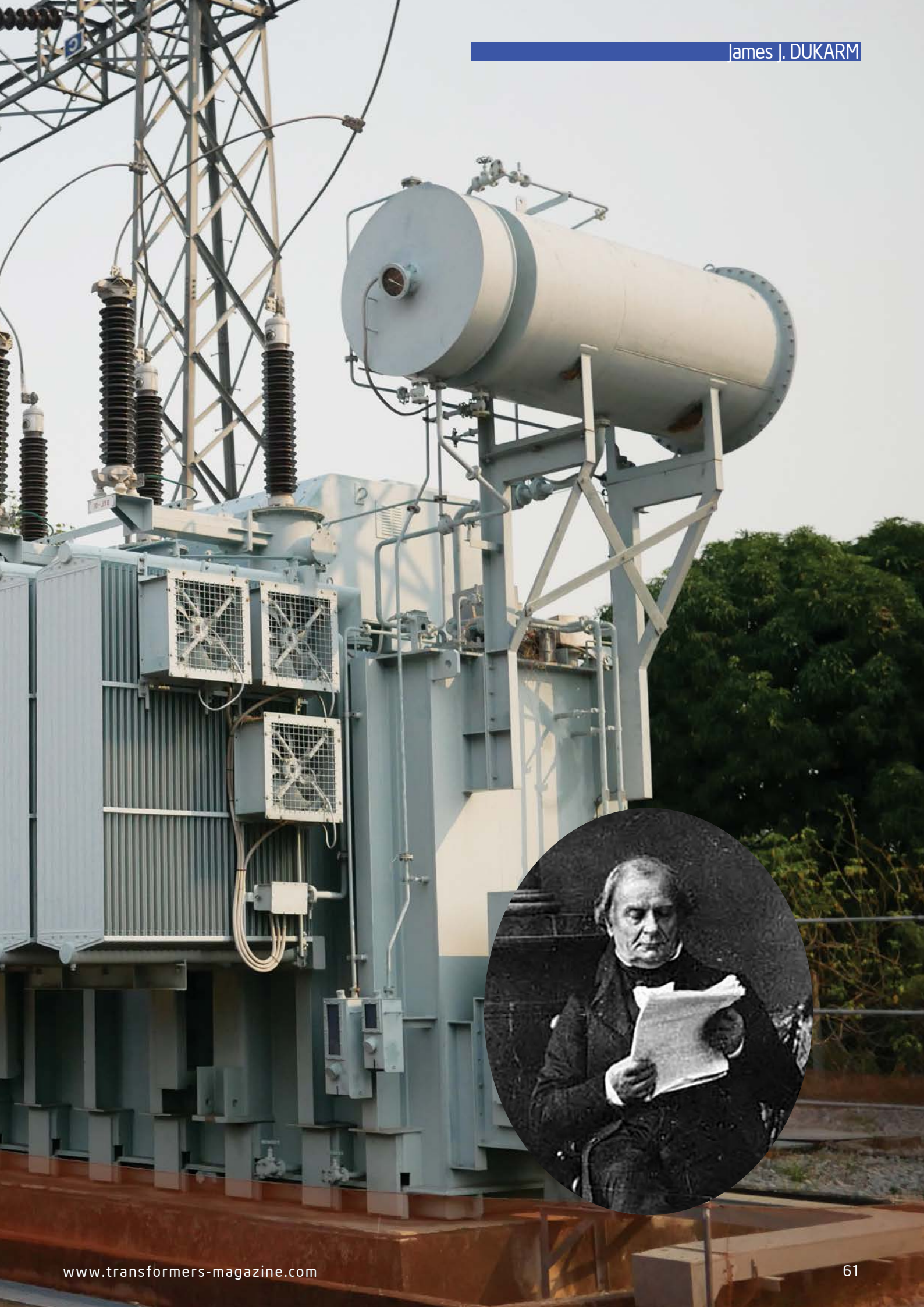
ABSTRACT

Dissolved gas analysis (DGA) is a non-invasive screening and diagnostic method for liquid-insulated power transformers. The basic gas laws underlying common calculations used for DGA interpretation are derived and

explained from the ideal gas equation of state.

KEYWORDS:

DGA; ideal gas; mole fraction; partial pressure; partial volume, Dalton's law, Graham's law.



Transformer insulating oil is often specially refined mineral oil, but various synthetic oils, ester liquids, and silicone liquids are also used in transformers

1. The gas-oil-paper system of a transformer

Gases that may be found in an operating power transformer include oxygen, nitrogen, argon, and carbon dioxide from the air, as well as certain gases formed mainly by pyrolysis (thermal decomposition without oxidation) of solid and liquid insulation. Those include carbon monoxide, carbon dioxide, hydrogen, and light hydrocarbon gases. The extraction, measurement, and diagnostic interpretation of the gases dissolved in the insulating oil of a power transformer is called dissolved gas analysis (DGA).

A power transformer is usually contained in a steel main tank, in which any gas content is distributed between:

- Insulating oil (up to tens of thousands of liters);
- Oil-immersed thin cellulosic winding insulation is sometimes referred to concisely but inaccurately as paper insulation (up to several tons), and
- A gas space.

Transformer insulating oil is often specially refined mineral oil, but various synthetic oils, ester liquids, and silicone liquids are also used in transformers. The discussion in this article is very general and does not depend on any one type of insulating liquid.

The thin cellulosic winding insulation consists of

- Kraft paper wound tightly around conductors, and
- Thin (less than 3 mm thickness) press-board spacers and barriers.

The gas space is provided to allow the oil to expand and contract in response to changing temperatures without rupturing or buckling the main tank. Some power transformers have a conservator tank mounted on top and connected to the main tank by a vertical pipe. In such

transformers, the main tank is completely full of oil, and the gas space is above the oil in the conservator. Otherwise, the gas space is a gas blanket above the oil in the main tank.

The volumetric thermal expansion coefficient of transformer oil is approximately 0.0008 per kelvin [1]. For example, if the transformer's temperature rise from cold start at ambient temperature to full rated load is 65 degrees, the resulting fractional increase in oil volume over that range is about $0.0008 \times 65 = 0.052$, or 5.2%. The designed volume of the gas space depends on details of tank construction, oil protection system, and operating temperature range, but it must be large enough to maintain tolerable gas pressure during normal operation without having to release gas or take in air.

A power transformer has an oil protection system whose purpose is to minimize the gas space's content of oxygen and water, which dissolve in the oil and participate in chemical reactions that degrade the liquid and solid insulation. There is a spectrum of possibilities for the oil protection system:

- Open breather - the free exchange of gases and moisture between the atmosphere and the gas space;
- Desiccant breather - exchange of gases between the atmosphere and the gas space through a desiccant, removing most of the water content;
- Conservator with a diaphragm - free breathing into the conservator, but with a rubber bag or diaphragm separating the gas space from the oil, preventing exposure of the oil to air and moisture;
- Sealed - closed system with vacuum and pressure relief valves to admit air into or expel gas from the gas space as required to avoid extreme conditions;
- Nitrogen-regulated system - with overpressure relief and pure dry nitrogen injected as required to maintain a

slight positive pressure (relative to atmospheric) in the gas space.

Each type of oil protection system has its own implications regarding the interpretation of dissolved gas levels in the oil.

2. The ideal gas equation of state

2.1 Gas variables

For the technical discussion of gases in transformers, it is useful to consider the transformer as a thermodynamic system, in which heat and energy flow and changes in gas distribution between the gas space, the oil, and the thin cellulosic insulation are of interest. The relevant principal thermodynamic state variables, with corresponding SI units [2], are:

- **Volume** (V , cubic meters) One cubic meter is a kiloliter, that is, 1000 liters.
- **Pressure** (P , pascals) One atmosphere (atm) is 101,325 Pa or 101.325 kPa.
- **Temperature** (T , kelvins) A kelvin is one Celsius degree. The freezing point of water at one atmosphere of pressure is 273.15 K. The relationship between Celsius temperature and Kelvin temperature is therefore $T_K = T_C + 273.15$.
- **Amount of a substance** (x , moles) The SI unit for the amount of a substance is the mole (mol), which is defined as $6.02214076 \times 10^{23}$ (the Avogadro number N_A) basic particles of the substance [3]. For compounds, the basic particles are molecules; for elements, atoms; in other cases, ions, electrons, or other specified particles are counted.
- **Mole fraction** (T , unitless) The mole fraction of substance number i in a mixture is $x_i = n_i/n$, where $n = n_1 + n_2 + \dots + n_k$ is the number of moles of the mixture.
- **Molar mass** (kg/mol) The molar mass of a substance is the average mass of one mole of the substance, considering the terrestrial distribution of isotopes of the relevant elements. It is the average number of nucleons in one molecule of the substance, multiplied by one gram of mass. Although the SI units are in kilograms per mole, the usual practice is to express the molar mass as grams per mole.

All the formulas and equations discussed below employ SI units for the relevant

variables and constants, except where explicitly stated otherwise.

Fractions as percentages. Some humans seem to be allergic to fractions unless they are expressed as percentages. In calculations involving fractions, the insistence on expressing every fraction as a percentage provides the opportunity for error and confusion by the proliferation of factors and divisors of 100 in the intermediate steps of the calculation. To avoid that, we do not convert fractions to percentages except for results intended for display and reporting, where the relevant variable expressed as a percentage will have a per cent sign appended to its name.

2.2 Spherical cows and ideal gas

A gas law is a mathematical model (usually a formula) describing the relationship between various gas properties and behaviors. An old joke about scientific modeling concerns a simplifying assumption in some model that cows are spherical. One spherical cow commonly encountered in physics and chemistry is the *ideal gas*, whose molecules are so small and inert that they behave like billiard balls in outer space – in particular, they do not repel each other or clump together. An ideal gas cannot be liquefied. The assumption that gases are ideal is appropriate and convenient for transformer DGA because in an operating transformer the concentrations of non-atmospheric gases in the oil are very small, gas space pressure is close to atmospheric, and internal temperatures are moderate.

The mother of all gas laws, attributed to B. P. E. Clapeyron¹ [4], is the *ideal gas equation of state*, which explains how, for an ideal gas, the thermodynamic state variables n, P, T, V named above relate to each other at equilibrium. It is

$$PV = nRT \quad (1)$$

where P is pressure in pascals, V is volume in cubic meters, n is the number of moles of gas, T is temperature in kelvins, and the molar gas constant R is $N_A k_B$, where the Boltzmann constant k_B is exactly $1.380649 \times 10^{-23} \text{ J K}^{-1}$ [2]. The value of R is therefore exactly $8.31446261815324 \text{ J K}^{-1} \text{ mol}^{-1}$.

¹ Benoît Paul Émile Clapeyron (1799-1864), a French physicist and engineer, was one of the principal founders of thermodynamics.

The transformer can be considered a thermodynamic system in which heat and energy flow and changes in gas distribution between the gas space, the oil, and the thin cellulosic insulation are of interest

Note that PV is energy expressed in joules. The ideal gas equation of state is unchanged, and PV and R have the same respective numerical values, if pressure is expressed in kilopascals and volume is in liters, since

$$J = \text{Pa} \cdot \text{m}^3 = \text{kPa} \cdot \text{L} \quad (2)$$

A simple consequence of the ideal gas equation is that for any fixed amount of a gas, the quantity PV/T is constant. That relationship is useful for predicting the effect on one variable of changes in the other two variables. For example, what happens to the gas pressure in the gas space when the transformer is de-energized and the gas space cools down from 90°C to 25°C ? Let P_1 be the initial and P_2 be the final gas pressure, and let $T_1 = 90 + 273.15 = 363.15 \text{ K}$ and $T_2 = 25 + 273.15 = 298.15 \text{ K}$. Furthermore, let V_1 be the initial volume of the gas space, and let $V_2 = 1.04 V_1$ be the volume of the gas space after thermal contraction of the oil. Then

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

So

$$\frac{P_2}{P_1} = \frac{V_1}{V_2} \frac{T_2}{T_1} = \frac{V_1}{1.04 V_1} \frac{298.15}{363.15} = 0.789.$$

That is, the cooling of the transformer reduces the gas space pressure by 21% unless gas (such as nitrogen or air) is added.

3. Gas mixtures

3.1 Mole fractions

Consider a mixture G of ideal gases G_i for $i = 1, 2, \dots, k$. For each i , the amount of G_i is n_i so the amount of G is $n_G = n_1 + \dots + n_k$. Since the mixture G and all its components are ideal gases, from the point of view of the ideal gas law (1) they are all indistinguishable except for their amounts. For example, the components could be hydrogen, methane, and other chemically distinct gases; or they could all be nitrogen, with each G_i being a

quantity of nitrogen added to G on a different date.

A natural way to characterize a gas mixture without specifying amounts is to specify the *mole fractions* of the components. For each i , $x_i = n_i/n_G$, and of course

$$x_G = \frac{n_G}{n_G} = 1 = x_1 + \dots + x_k.$$

For example, the composition of pure dry air is approximately 0.78 nitrogen, 0.21 oxygen, and 0.01 argon. Those numbers are mole fractions. Note that the mole fraction of a component of a gas mixture is independent of temperature and pressure. Hot or cold, rarified or compressed, dry air has the same mole fractions of nitrogen, oxygen, and argon as at one atmosphere and 0°C .

It is common for the mole fractions of gases in a mixture to be expressed as percentages. For example, dry air is approximately 78% nitrogen. Likewise, it is common for a trace component of a gas mixture to be quantified as a mole fraction in units of micromoles of gas per mole of mixture ($\mu\text{mol/mol}$) or alternatively parts per million (ppm), to avoid dealing with tiny fractions or small fractions of a percent. For example, the mole fraction of carbon monoxide in the air in a factory might be 0.000015, which could be expressed as 0.0015% or 15 ppm.

3.2 Dalton's law of partial pressures

Suppose a sample of gas mixture is in a container of volume V at temperature T and pressure P . Each gas G_i in the mixture is ideal, occupies the full volume V , has the same temperature T , and (not interacting in any way with the other components) exerts a proportional share of the total pressure $x_i P = P_i$, called its *partial pressure*, on the surroundings in accordance with the ideal gas law (1):

Mole fraction and fractional pressure and volume are invariant under changes of pressure and volume, but gas concentrations (like partial pressures and volumes) are not

$$P_i V = (x_i P) V = x_i n R T = n_i (R T).$$

Rearranging the equation slightly:

$$P V_i = P (x_i V) = x_i n R T = n_i (R T),$$

we see that at total pressure P (not P_i), the component G_i by itself can be imagined as occupying a proportional share $V_i = x_i V$ of the total volume, called its *partial volume*. Note that the partial volume is hypothetical since every component of the mixture G is spread out through the full volume V of the mixture. The partial volume V_i is the volume that gas G_i would occupy at the given temperature T and pressure P if there were no other gases present.

Dalton's² law of partial pressures states that the pressure P of a mixture of k ideal gases is the sum of the partial pressures of those gases:

$$P = x_1 P + x_2 P + \dots + x_k P = P_1 + P_2 + \dots + P_k \quad (3)$$

where for each i is the mole fraction of gas i in the mixture. Likewise, the volume V of a mixture of ideal gases is the sum of the partial volumes of those gases:

$$V = x_1 V + x_2 V + \dots + x_k V = V_1 + V_2 + \dots + V_k \quad (4)$$

3.3 Mole fraction and fractional partial pressure

The partial pressure of gas i in a mixture, defined above as $P_i = x_i P$, is a pressure. Just as the mole fraction $x_i = n_i/n$ is the unitless ratio of the amount n_i of compo-

nent i to the total amount n of the mixture, it is useful to define the unitless *fractional partial pressure* $p_i = P_i/P$ and *fractional partial volume* $v_i = V_i/V$. It is easy to see that all three of these fractional quantities are equivalent, since

$$p_i = \frac{P_i}{P} = \frac{x_i P}{P} = x_i$$

And

$$v_i = \frac{V_i}{V} = \frac{x_i V}{V} = x_i$$

Mole fraction x_i and its aliases fractional partial pressure p_i and fractional partial volume v_i are unitless and invariant under changes of temperature, volume, and pressure if the total amount n of gas is constant. Thus, for example, the mole fraction or fractional partial pressure of an individual gas in the gas space of a transformer can be calculated – without knowing the pressure, temperature, or volume of the gas space – using gas analysis data reported by the laboratory at standard temperature and pressure.

Notational warning. Since mole fraction is equivalent to fractional partial volume, ppm mole fraction is the same as ppm fractional partial volume. This gets confusing when ppm, $\mu\text{mol/mol}$, and $\mu\text{L/L}$ are used in connection with gas concentrations (discussed in the next part of this series) in gas or liquid, where a gas partial volume reduced to standard temperature and pressure is compared with a standard volume. Mole fraction and fractional pressure and volume are invariant under changes of pressure and volume,

but gas concentrations (like partial pressures and volumes) are not!

3.4 Graham's law of gas diffusion and effusion

Both sides of the ideal gas equation of state (1) represent energy. Using that equation, we can calculate the average energy per molecule, which is average energy per mole PV/n divided by Avogadro's number N_A . From (1) we can also see that the energy is proportional to the absolute temperature T . There is no molecular potential energy because the molecules of an ideal gas do not attract or repel each other. Therefore, pressure and temperature are expressions of average molecular kinetic energy, that is, thermal energy.

In a mixture of k gases, all gases have the same temperature and volume, but each has its own partial pressure P_i and amount n_i . The average molecular kinetic energy of gas i is

$$E_i = \frac{P_i V}{n_i N_A}$$

How does that compare with the average kinetic energy $E = (PV)/(nN_A)$ of all the gas molecules? Consider this:

$$\begin{aligned} \frac{E_i}{E} &= \frac{(P_i V)/(n_i N_A)}{(PV)/(nN_A)} = \frac{P_i V}{n_i N_A} \frac{nN_A}{PV} \\ &= \frac{P_i}{P} \frac{n}{n_i} = \frac{p_i}{x_i} = 1 \end{aligned} \quad (6)$$

since $p_i = x_i$. Therefore, the average molecular kinetic energy of each gas i is the same as the average molecular kinetic energy of all the gas. The average kinetic energy of gas molecules is related to molecular mass and average velocity by the Newtonian formula

$$E = \frac{mv^2}{2}. \quad (7)$$

Since all the gases in a mixture have the same average molecular kinetic energy, for any two of the gases we can say that

$$\frac{m_1 v_1^2}{2} = \frac{m_2 v_2^2}{2} \quad (8)$$

Solving to compare the average velocities:

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}} \quad (9)$$

At this point we make a small leap and consider that the average velocity of gas

Graham's law states that the rates of diffusion and effusion of a gas are inversely proportional to the square root of the molecular mass

² John Dalton (1766-1844) was a physicist.

molecules moving freely must be proportional to their average rates of diffusion (bulk spreading) and effusion (escape through a narrow passage). The statement that the rates of diffusion and effusion of a gas are inversely proportional to the square root of the molecular mass is called Graham's³ law.

3.5 Standard temperature and pressure

According to (1), for an ideal gas V is directly proportional to n if T and P are controlled:

$$V = n \frac{RT}{P}$$

In other words, the amount n of gas can be quantified in terms of volume if standard reference values for temperature and pressure are specified. For analysis of gases in transformer oils, there are at least two major published standards, ASTM D3612 [5] and IEC 60567 [6], upon which numerous national and regional standards are based. The reference temperature and pressure used by each for reporting volumetric dissolved-gas concentrations are shown in Table 1. The corresponding ideal gas standard molar volume V_m° shown for each was calculated based on (1) with $n = 1$ and using the respective standard values for temperature and pressure:

$$V_m^\circ = \frac{RT^\circ}{P^\circ} \quad (10)$$

Any amount n of gas can be represented by a partial volume V at standard pressure and temperature:

$$n = \frac{P^\circ V}{RT^\circ} = \frac{V}{V_m^\circ} \quad (11)$$

So

$$nV_m^\circ = V.$$

This relationship is useful for DGA because all DGA data reported by the laboratory are reduced to specified standard temperature and pressure.

Bibliography

[1] Z. Nadolny and G. Dombek, *Thermal properties of mixtures of mineral oil*

³ Thomas Graham (1805-1869) was a physical chemist.

All DGA data reported by the laboratories are reduced to specified standard temperature and pressure

and natural ester in terms of their application in the transformer," E3S Web of Conferences, 19:01040, Jan 2017.

[2] BIPM, *SI Brochure: The International System of Units (SI)*, 9th ed. Bureau Internationale des Poids et Mesures, 2019. [Online]. Available: <https://www.bipm.org/en/publications/si-brochure>

[3] "mole," in *IUPAC Compendium of Chemical Terminology*, 3rd ed. International Union of Pure and Applied Chemistry (IUPAC), 2019. [Online]. Available: <https://doi.org/10.1351/goldbook.M03980>

[4] B. P. E. Clapeyron, *Memoire sur la puissance motrice de la chaleur*, Journal de l'Ecole Polytechnique, vol. XIV, pp. 153–90, 1834.

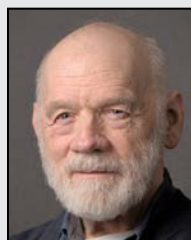
[5] ASTM D27, *Standard Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography*. ASTM International, 2017, ASTM D3612-02(2017).

[6] *Oil-filled electrical equipment — Sampling of free gases and analysis of free and dissolved gases in mineral oils and other insulating liquids – Guidance*, 5th ed. International Electrotechnical Commission, Dec 2023, IEC 60567:2023.

Table 1. Reference values for temperature and pressure, with corresponding standard molar gas volume

Standard	T° (K)	P° (kPa)	V _m [°] (L)
ASTM D3612-02	273,15	101,325	22,414
IEC 60567:2013	293,15	101,325	24,055

Author



James J. Dukarm completed a PhD in mathematics in 1980 and left academia to work in robotics and industrial software. He is the founder and Principal Scientist of Delta-X Research Inc. in Victoria BC Canada, which supplies power transformer monitoring and diagnostic software for electric power systems. Prior to starting Delta-X Research in 1992, he founded and operated a company that developed very advanced industrial software solutions on contract, including voice controls for graphical workstations, a factory switchgear monitoring system, a transformer bushing replacement expert system, and the first commercial software product for insulation power factor testing. Jim has been an active participant in DGA-related working groups of the IEEE PES Transformers Committee.