


Pressure of real gas vs ideal gas

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Pressure of real gas vs ideal gas

What is perfect gas and ideal gas. What is difference between real and ideal gas. What is ideal and real gas. Why ideal gas deviate from real gas.

Deviations from Ideal Gas Law Behavior Van der Waals Equation Analysis of the van der Waals Constants Van der Waals Equation The behaviour of real gases usually agrees with the forecasts of the ideal gas equation within 5% at normal temperatures and pressures. At low temperatures or high pressures, real gases differ significantly from the behaviour of the ideal gas. In 1873, while seeking a way to connect the behaviour of liquids and gases, the Dutch physicist Johannes van der Waals developed an explanation for these deviations and an equation that can adapt to the behaviour of real gases on a much wider range of pressures. Van der Waals realized that two of the hypotheses of kinetic molecular theory were questionable. The kinetic theory assumes that gas particles occupy a negligible fraction of the total volume of gas. It also assumes that the adhesive force between gas molecules is zero. The first hypothesis works at pressures near 1 atm. But something happens to the validity of this hypothesis as the gas is compressed. Imagine for the moment that atoms or molecules in a gas were all grouped into a cylinder angle, as shown in the figure below. At normal pressures, the volume occupied by these particles is a negligible small fraction of the total volume of the gas. But at high pressure, this is no longer true. As a result, real gases are not compressible to high pressures as an ideal gas. The volume of a real gas is therefore larger than expected by the ideal equation of high pressure gas. Van der Waals proposed to correct the fact that the volume of a real gas is too large at high pressures by subtracting a term to the volume of the real gas before replacing it in the equation of the ideal gas. It introduced a constant (b) constant constant in the equation of the ideal gas which was equal to the volume actually occupied by a mass of gas particles. Since the volume of gas particles depends on the number of gas molecules in the container, the term which is removed from the real volume of the gas is equal to the number of gas times b. $P(V - nb) = nRT$ When the pressure is relatively small, and the volume is reasonably large, the term nb is too small to make any difference in the calculation. But at high pressures, when the volume of the gas is small, the term nb corrects the fact that the volume of a real gas is greater than expected by the equation of the ideal gas. The hypothesis that there is no force of attraction between the gas particles cannot be true. If so, the gases would never have been able to form liquids. Actually, there is a small force of attraction among gas molecules that tends to hold molecules together. This force of attraction has two consequences: (1) gases condense to form liquids at low temperatures and (2) the pressure of a real gas is sometimes smaller than expected for a gas. Correcting for the fact that the pressure of a real gas is smaller than expected van der Waals added a term to the pressure in this equation. This term contained a second constant (a) and has the form: a/n^2 . The whole van der Waals equation is written as follows. This equation is a kind of mixed blessing. It provides a much better adaptation with the behaviour of a real gas than the ideal gas equation. But it does at the price of a general loss. The ideal equation for gases is equally valid for any gas, while the van der Waals equation contains a pair of constants (a and b) changing from gas to gas. The ideal equation of the gas provides that a PV chart compared to P for a gas is a horizontal line because the PV should be a constant. The experimental data for photovoltaics compared to P for gases H₂ and N₂ to 0°C and CO₂ to 40°C are shown in the following figure. The values of van der Waals constants for these and other gases are shown in the table below. Van der Waals for various gases Composed at (L²-atm/mol²) b (L/mol) He 0.03 412 0.02 370 Ne 0.2107 0.01 709 H₂ 0.2444 0.02 661 Ar 1.345 0.03 219 O₂ 1.360 0.03 803 N₂ 1.390 0.03 913 CO 1.485 0.03 985 CH₄ 2.253 0.04 278 CO₂ 3.592 The extent of deviations from the ideal behavior of gas can be illustrated by comparing the results of calculations made using the ideal equation of gas and van der Waals equation for 1.00 CO₂ to 0°C in containers of different volumes. Let's start with a 22.4 litre container. According to the ideal gas equation, the pressure of this gas should be 1.00 atm. By substituting what we know about CO₂ in the van der Waals equation you get a much more complex equation. However, this equation can be resolved by gas pressure. $P = 0.995$ atm At normal temperatures and pressures, the ideal equations of gas and van der Waals essentially give the same results. We now repeat this calculation, assuming that the gas is compressed in order to fill a container that has a volume of only 0.200 liters. According to the ideal gas equation, the pressure should be increased to 112 atm to compress 1.00 m of CO₂ to 0°C at a volume of 0.200 L. The van der Waals equation, however, provides that the pressure will have to increase to 52.6 atm to obtain the same results. $P = 52.6$ atm With the increase of CO₂ pressure, the van der Waals equation initially gives lower pressure than the ideal gas equation, as shown in the figure below, due to the strong attraction force between CO₂ molecules. A pressure product chart multiplied by the volume of H₂, N₂, CO₂ gas samples compared to the pressure of these gases. We buy even more gas, increasing the pressure to reach a volume of only 0.0500 liters. The ideal equation provides that the pressure should increase to 448 atm to condense 1.00 CO₂ to 0°C at a volume of 0.0500 L. The van der Waals equation predicts that pressure will have to reach 1620 atm to achieve the same results. $P = 1620$ atm Van der Waals equation Waalshigher than the ideal gas equation at very high pressures, as shown in the figure above, due to the volume occupied by the CO₂ molecules. Analysis of van der Waals constants The van der Waals equation contains two constants, a and b, which are characteristic properties of a particular gas. The first of these constants corrects the adhesive force between the gaseous particles. Compounds for which the adhesive force between particles is strong have high values for a. If you think about what happens when a liquid boils, you might expect compounds with higher values of a to have higher boiling points. (As the adhesive force between the gaseous particles becomes stronger, we have to go to higher temperatures before we can break the bonds between the molecules in the liquid to form a gas.) It is not surprising to find a correlation between the value of the constant a in the van der Waals equation and the boiling points of a number of simple compounds, as shown in the figure below. Gases with very small values of a, such as H₂ and He, must be cooled to near-absolute zero before condensing into a liquid. The other van der Waals constant, b, is an approximate measure of the size of a gas particle. According to the table of van der Waals constants, the volume of a mole of argon atoms is 0.03 219 litres. This number can be used to estimate the volume of a single argon atom. The volume of an argon atom can then be converted into cubic centimeters using the appropriate unit factors. Assuming the argon atoms are spherical, we can estimate their radius. Let's start by observing that the volume of a sphere is related to its radius by the following formula. $V = 4/3 r^3$ Suppose the volume of an argon atom is 5.345×10^{-23} cm and calculate the radius of the atom. $r = 2.3 \times 10^{-8}$ cm According to this calculation, an argon atom has a radius of about 2×10^{-8} cm. Although the ideal gas model is very useful, it is only an approximation of the true nature of gases, and the equations derived from its assumptions are not entirely reliable. As a result, the measured properties of a real gas very often differ from those predicted by our calculations. Let's take a look at some of the reasons for these discrepancies. Low Temperature and Real Gas Pressure Imagine riding an H₂O molecule in water vapour heated to a relatively high temperature. (The term vapour is commonly used to describe a gas derived from a substance that is a liquid at normal temperatures and pressures.) When your H₂O molecule passes close to one another, the two particles can be attracted to each other. As long as the temperature remains high, however, fast-moving water molecules break the attraction almost immediately and continue on their separate paths. As the of a high-temperature gas only spend a small fraction of their time experimenting with these short-term attractiveness, duration, of the attractions on the properties of the gas is negligible. We can therefore consider a high-temperature gas as an ideal gas, without attraction between particles. When the temperature of the water vapour decreases, the water molecules move slower, making it harder for them to break the attractiveness that forms between them. Thus the particles of a gas at a lower temperature spend a greater part of their time attracted by other particles. The ideal gas model is based on the assumption that there are no significant attractions between the particles. Thus, the lower the temperature, the less a gas behaves like an ideal gas. When the attractions between its particles are significant, the measured pressure of a real gas is less than that predicted by the ideal gas equation. $P_{real} =$ measured pressure $P_{ideal} =$ pressure calculated from the ideal gas equation and measured n, T and V $P_{real} < P_{ideal}$ To understand why the actual pressure is less than the predicted ideal pressure, imagine yourself straddling a gas particle at the instant before it hits a wall of its container. In that instant, there are more particles behind your particle than in front of it. In an ideal gas with no attractions between particles, your particle would hit the wall with a force that depends only on the mass and velocity of the particle. In a real gas, however, the attractions between the particles will pull your particle back toward the center of the container, slow it down, and decrease the force of its collision with the wall (Figure 1). By decreasing the force of the collisions of the gaseous particles against the walls, the gas pressure decreases. Thus the pressure of a real gas, with attraction between the particles, will be lower than that expected for an ideal gas, without attraction between the particles. The lower the temperature of a gas, the greater the attraction between the particles, and the greater the actual or measured pressure that deviates from the pressure predicted by the ideal gas equation. Figure 1: $P_{real} < P_{ideal}$ In a real gas there are attractions between the particles. Just before a particle collides with a wall of its container, the particles behind it retract it, decreasing its velocity and decreasing the force of its collision. Increase in the Concentration and Actual Gas Pressure The concentration of a gas (gas molecules per unit volume) can be increased in two ways: (1) by decreasing the volume or (2) by adding more gas to a given volume. The higher the concentration of the gas, the smaller the mean distance between the particles; and if the particles are closer to each other, a greater number of them will be close enough to notice a significant attraction to each other (Figure 2). Thus, even if the pressure of a real gas increases with increasing concentration, it does not rise as if there were no between the particles. with a greater of gas, there are more particles pulling a particle back to the center of the container instantly before it hits the wall. This greater attraction in the direction away from the wall decreases pressure against the walls than what would be if there were fewer attractions among the particles (Figure 13.3) Figure 2: Increased gas concentration leads to a greater difference between real pressure and ideals The greater the number of particles per unit volume, the greater the number of significant attractions between a particle just before it hits the wall and the particles behind it. This leads to a greater push towards the center of the container and a greater difference between the real, measured pressure and the ideal pressure, calculated. Figure 3: Because the actual pressure deviates from the ideal pressure increases the concentration and the real volume of the gas When a gas behaves like an ideal gas, we can calculate its volume by measuring its temperature, pressure and mass and connecting it to the ideal gas equation. When the concentration of a gas is very high, however, the actual or measured volume is greater than the volume that would be calculated by the equation of the ideal gas. The reason is that small as the particles of a gas are, they constitute part of its volume. In other words, the real volume of a gas is equal to the volume that the particles themselves occupy more the volume of empty space between the particles. $V_{real} = V_{particles} + V_{empty}$ One of the preconditions of the ideal gas model is that the volume occupied by particles is negligible, so the ideal volume is equal to the volume of empty space. However, since the particles of a real gas occupy a finite volume, the actual or measured volume of a gas is larger than the ideal volume calculated by the equation of the ideal gas. $V_{ideal} = V_{empty}$ $V_{real} = V_{particles} + V_{empty} = V_{particles} + V_{ideal}$ $V_{real} > V_{ideal}$ Since the concentration of a gas increases, both because more gas has been added to the same volume or because the gas has been compressed in a smaller volume, the percentage of the volume occupied by the particles increases. This leads to a greater difference between the actual volume, measured and the ideal volume calculated (Figure 4). Figure 4: Effect of concentration on real volume compared to ideal volume

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