

Answer on Question #84940 – Chemistry – General Chemistry

Real gases deviate from the ideal gases at high pressures and low temperatures. Real equations of state account for these deviations within the format of the equation. Which part of the VDW equation of state corrects for low temperature deviations?

Solution:

Van der Waals proposed that we correct for the fact that the volume of a real gas is too large at high pressures or low temperature by subtracting a term from the volume of the real gas before we substitute it into the ideal gas equation. He therefore introduced a constant (b) into the ideal gas equation that was equal to the volume actually occupied by a mole of gas particles. Because the volume of the gas particles depends on the number of moles of gas in the container, the term that is subtracted from the real volume of the gas is equal to the number of moles of gas times b .

$$P(V - nb) = nRT$$

When the pressure is relatively small, and the volume is reasonably large, the nb term is too small to make any difference in the calculation. But at high pressures or low temperature, when the volume of the gas is small, the nb term corrects for the fact that the volume of a real gas is larger than expected from the ideal gas equation.

The assumption that there is no force of attraction between gas particles cannot be true. If it was, gases would never condense to form liquids. In reality, there is a small force of attraction between gas molecules that tends to hold the 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 an ideal gas.

To correct for the fact that the pressure of a real gas is smaller than expected from the ideal gas equation, van der Waals added a term to the pressure in this equation. This term contained a second constant (a) and has the form: an^2/V^2 . The complete van der Waals equation is therefore written as follows.

$$\left[P + \frac{an^2}{V^2} \right] (V - nb) = nRT$$

This equation is something of a mixed blessing. It provides a much better fit with the behavior of a real gas than the ideal gas equation. But it does this at the cost of a loss in generality. The ideal gas equation is equally valid for any gas, whereas the van der Waals equation contains a pair of constants (a and b) that change from gas to gas.