Introduction to Physical Chemistry

2. Real Gases and van der Waals Equations

Two assumptions of Ideal Gas

The gas laws and kinetic molecular theory assume that:

1. molecules in the gaseous state do not exert any force, either attractive or repulsive, on one another.
2. The volume of molecules is negligibly small compared with that of container

This two conditions is said to exhibit **ideal behavior**

Deviations From Ideality

Assumptions of Ideal Gas Law

1. no attractive or repulsive forces
2. V of molecules negligible

Problems

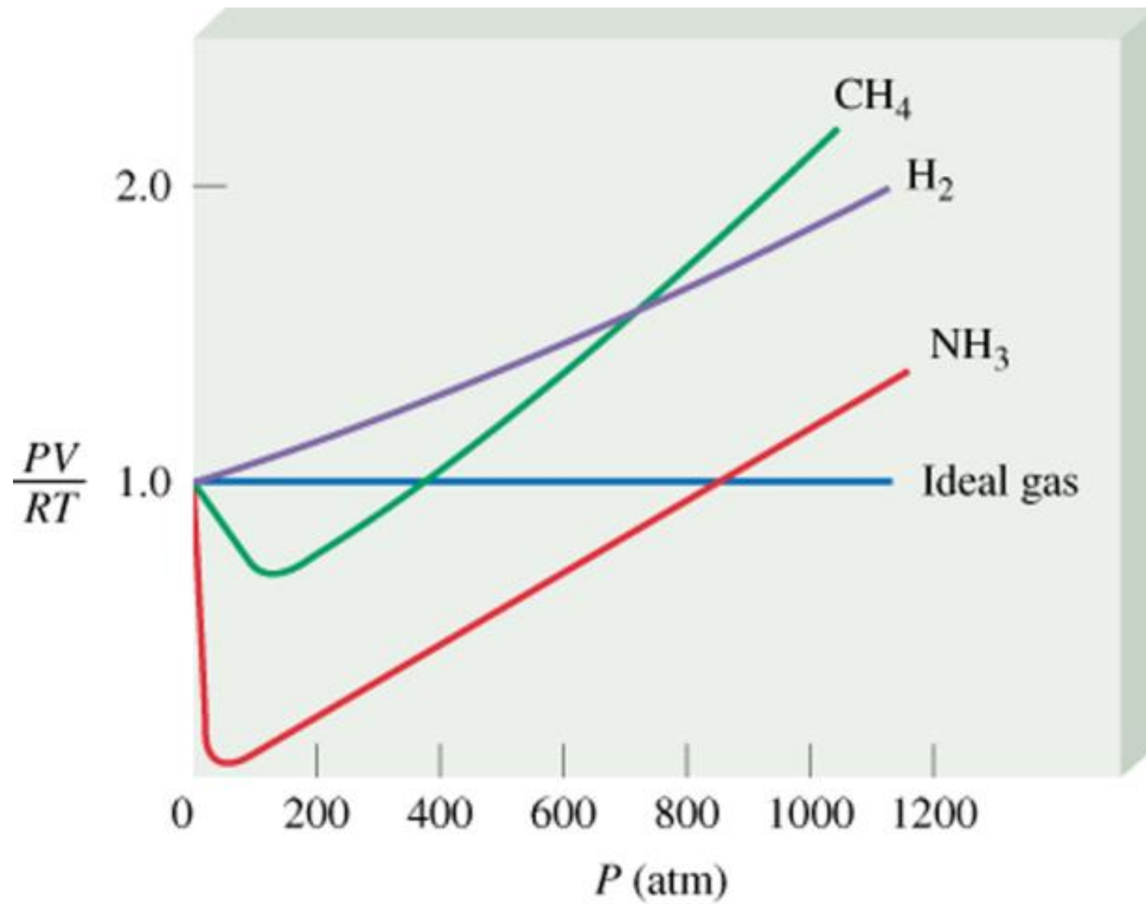
1. w/o intermolecular forces cannot condense gas to liquid
2. molecules of real gas occupy space

Deviations From Ideality (T = 0ºC)

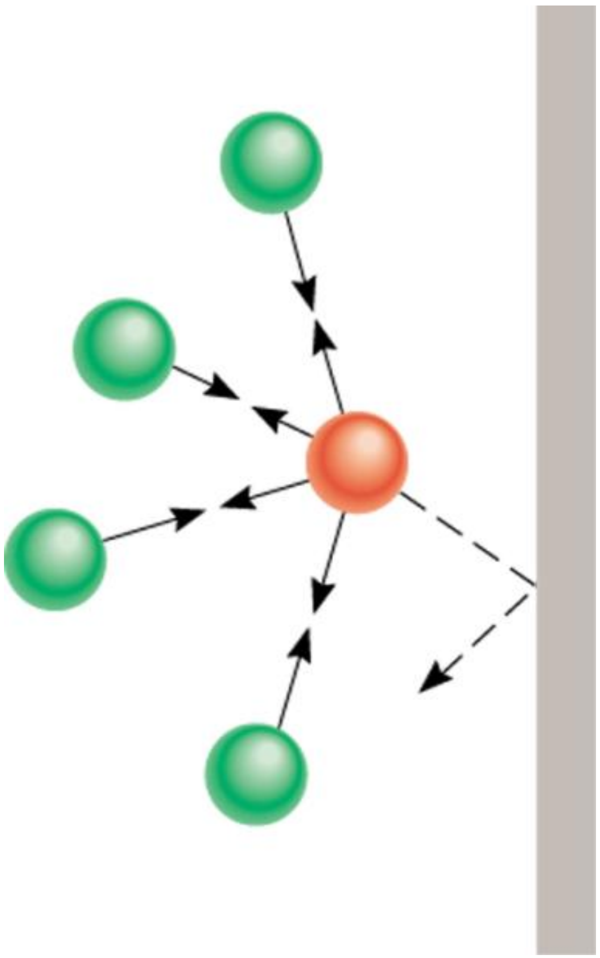
1 mol of ideal gas

$PV = nRT$

$$n = \frac{PV}{RT} = 1{,}0$$



Effect of intermolecular forces on the pressure exerted by a gas.



The speed of a molecule that is moving toward the container wall (red sphere) is reduced by the attractive forces exerted by its neighbors (gray spheres). Consequently, the impact this molecule makes with the wall is not as great as it would be if no intermolecular forces were present.

In general, the measured gas pressure is lower than the pressure the gas would exert if it behaved ideally.

Deviations from Ideal Behaviour

Ideal Gas Equation $PV = nRT$

- Look at assumptions for ideal gas
  - Real gas molecules do attract one another.

    (i.e., $P_{id} = P_{obs}$ + constant).
  - Real gas molecules do not occupy an infinitely small volume (they are not point masses).

    ($V_{id} = V_{obs}$ - const.)

The Van der Waal's Equation

$V_{id} = V_{obs} - nb$

where b is a constant for specific different gases.

$P_{id} = P_{obs} + a\,(n / V)^2$

where a is also different for different gases.

Ideal gas Law $P_{id} V_{id} = nRT$

van der Waals Equation

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

Two constants (a, b) that are experimentally determined for each separate gas

Van der Waals Constants of Some Common Gases

Gas	a $\left(\frac{atm \cdot L^2}{mol^2}\right)$	b $\left(\frac{L}{mol}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0371
H_2O	5.46	0.0305

Exercise

Given that 3.5 moles of NH_3 occupy 5.20 L at 47^0C, calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the van der Waals equation.

(a) We have the following data:

V = 5.20 L

T = (47 + 273) K =320 K

n = 3.50 mol

R = 0.0821 L.atm/K.mol

Substituting these values in the ideal gas equation, we write

$$P = \frac{nRT}{V}$$

$$P = \frac{(3.5mol)(0.0821L.atm/K.mol)(320K)}{5.20L}$$

$$P = 17.7atm$$

Exercise cont'd

We need Equation (5.17). It is convenient to first calculate the correction terms in Equation (5.17) separately. From Table 5.4, we have

a = 4.17 atm.L^2/mol^2

b = 0.0371 L/mol

So that the correction terms for pressure and volume are

$$\frac{an^2}{V^2} = \frac{(4.17 atm.L^2/mol^2)(3.50 mol)^2}{(5.20 L)^2} = 1.89 atm$$

$$nb = (3.50 mol)(0.0371 L/mol) = 0.130 L$$

Finally, substituting these values in the van der Waals equation, we have

(P + 1.89 atm)(5.20 L – 0.130 L) = (3.50 mol)(0.0821 L.atm/K.mol)(320 K)

P = 16.2 atm

Conclusion

The van der Waals equation is a modification of the ideal gas equation that takes into account the non ideal behavior of real gases. Its corrects for the fact that real gas molecules do exert forces on each other and that they do have volume. The van der Waals constants are determined experimentally for each gas

Home Work

1. Using the data shown in Table 5.4, calculate the pressure exerted by 2.50 moles of CO_2 confined in a volume of 5.00 L at 450 K. Compare the pressure with that predicted by the ideal gas equation.

2. At 27^0C, 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

3. Give a comprehensive explanation to the graph in slide 4!