Thermodynamics Lecture Notes: Chapter 3

Michaela Hirschmann

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3 The Law of gases

The state of a gas depends on the volume (V), pressure (P), and temperature (T). The relation between the volume, pressure, temperature and mass of the gas is called an equation of state. The equation of state can be applied for a state in equilibrium, i.e. the pressure and temperature are uniform over the volume and do not change with time.

3.1 Ideal gas laws

Gas laws are:

- Boyle's law: PV is constant when T is kept constant, for a given quantity of gas.
- Charles's law: V is proportional to T (in Kelvin) when P is kept constant.
- Gay-Lussac's law: P is proportional to T (in Kelvin) when V is kept constant.
- Avogadro's law: Gasses with identical P, T and V contain the same number of molecules.

The first three laws lead to:

$$P \times V \propto T. \tag{1}$$

From the dimensional point of view,

$$P : \left[\frac{N}{m^2}\right], \quad V : [m^3] \tag{2}$$

thus

$$P \times V : [\text{Nm} = \text{Joule}] \tag{3}$$

has a dimension of energy.

3.2 The equation of state of ideal gas

By combining four laws, we introduce the following **equation of state for an "ideal" gas:**

$$PV = NkT \tag{4}$$

where N is the number of gas molecules and k is called Boltzmann constant given by

$$k = 1.38 \times 10^{-23} \text{J K}^{-1} \tag{5}$$

Let us recall the atomic mass unit, where $1u$ corresponds the mass of the ^{12}C divided by 12 and

$$1u = 1.6605 \times 10^{-27}\text{kg} = 1.6605 \times 10^{-24}\text{g}. \tag{6}$$

Therefore, in $12g$ of ^{12}C, there are

$$\frac{12g}{12 \times 1.6605 \times 10^{-24} g} = \frac{1}{1.6605 \times 10^{-24}} = 6.02 \times 10^{23} \equiv N_A \tag{7}$$

of ^{12}C atoms. N_A is called Avogadro's number. We introduce a new unit, called Mole, corresponding to N_A particles.

We can then rewrite the equation of state for ideal gas to be

$$PV = nRT \tag{8}$$

where,

$$R = N_A \times k = 8.314 \frac{J}{mol\ K} \tag{9}$$

is called the universal gas constant and

$$n = \frac{N}{N_A} mol \tag{10}$$

is the number of moles for a given gas.

Let us say that the mass of a gas molecule is r u. Then the mass of the gas for one mole can be calculated as

$$r \times N_A = \frac{r \times 1.6605 \times 10^{-24} g}{1.6605 \times 10^{-24} g} = r\text{g} \tag{11}$$

i.e. one mole is the quantity of gas, whose mass in gram is numerically equal to the molecular mass of that gas.

Examples:

- For Hydrogen gas (H_2) the atomic mass is 2.0 u (twice that of the hydrogen atoms), thus 1 mole of H_2 gas corresponds to 2 g.
- For Carbon dioxide (CO_2) the atomic mass is 44 u, thus 1 mole of CO_2 corresponds to 44g. So, 220 g of CO_2 is equal to 220/44 = 5 moles.

Exercises:

- **What is the volume of 1 mol of gas at room temperature?**
  The standard temperature, $T = 273K (\approx 0^\circ)$, and standard pressure, $P = 1.00$ atm $= 1.013 \times 10^5 N/m^2$: STP.

  The volume of 1.00 mole of any gas at STP, assuming that it behaves like an ideal gas, is given by:

  $$V = \frac{nRT}{P} = \frac{1mol \times 8.314 Nm/(mol\ K) \times 273K}{1.013 \times 10^5 Nm^{-2}} = 22.4 \times 10^{-3} m^2 \tag{12}$$

  or 22.4 liters. → does not depend on the type of gas!

- **What is the mass of a room full of air?**
  The mass of air in a room with a size of $5m \times 3m \times 2.5m$ at STP: the volume of the air in the room is $V = 5m \times 3m \times 2.5m = 37.5m^3$. Since 1 mol of an ideal gas at STP gives 22.4 litres, $37.5m^3$ of an ideal gas at STP corresponds to

  $$37.5/22.4 \times 10^{-3} = 1674 mol. \tag{13}$$

  The air is composed of 20% O_2 and 80% N_2. The atomic mass numbers for O and N are 16 and 14, respectively. The molecular mass of air is then given by

  $$0.2 \times (2 \times 16) + 0.8 \times (2 \times 14) = 28.8, \tag{14}$$

  i.e. 1 mole of air is 28.8 g. Therefore 1674 mole of air is 48.2 kg.

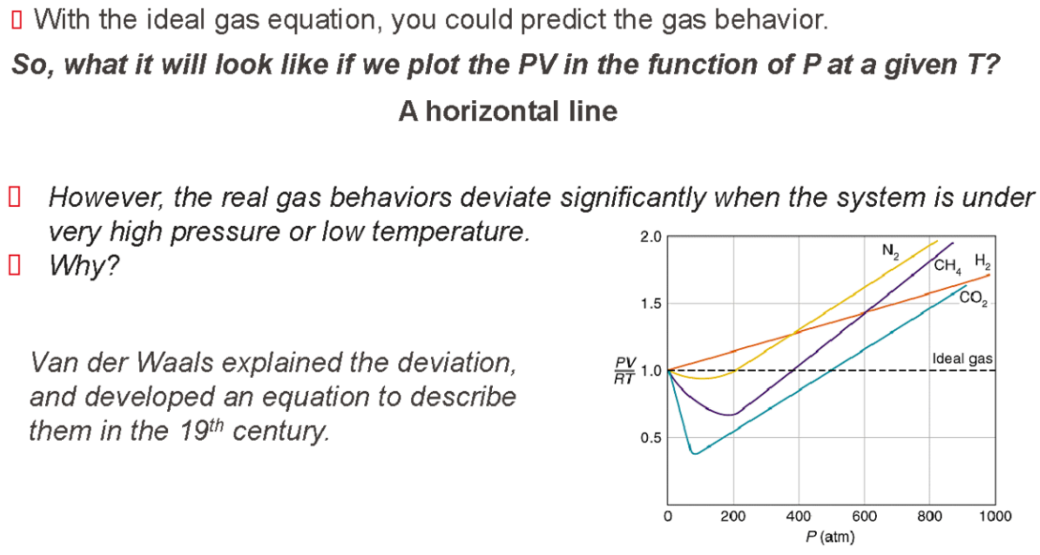
Let us assume that a system of ideal gas is in an equilibrium state with, (V_1, P_1, T_1), where

$$\frac{P_1V_1}{T_1} = nR. \tag{15}$$

We then change the same gas to a different equilibrium state (V_2, P_2, T_2). Since it is the identical gas to what was in the state of (V_1, P_1, T_1), nR remains constant. Thus, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{16}$$

3.3 Real Gases



- With the ideal gas equation, you could predict the gas behavior.

So, what it will look like if we plot the PV in the function of P at a given T?

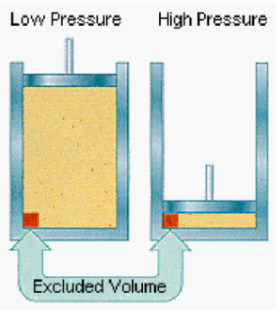
A horizontal line

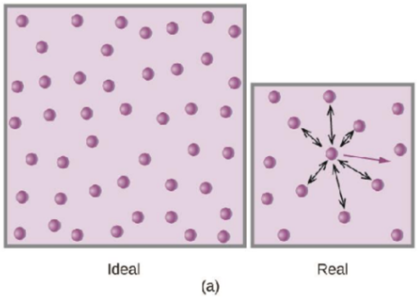
- *However, the real gas behaviors deviate significantly when the system is under very high pressure or low temperature.*
- *Why?*

Van der Waals explained the deviation, and developed an equation to describe them in the 19th century.

Ideal gas concept comes from the kinetic molecular theory. If we want to describe a real gas, two of the assumptions are questionable:

- *Gas molecules occupy a negligible volume compared to the gas volume*
- *Attraction force between gas molecules is zero*





Correction terms for real gases:

- Van der Waals Introduced a constant (***b***) for volume correction
- A second term (***a***) is introduced for pressure correction

$$P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

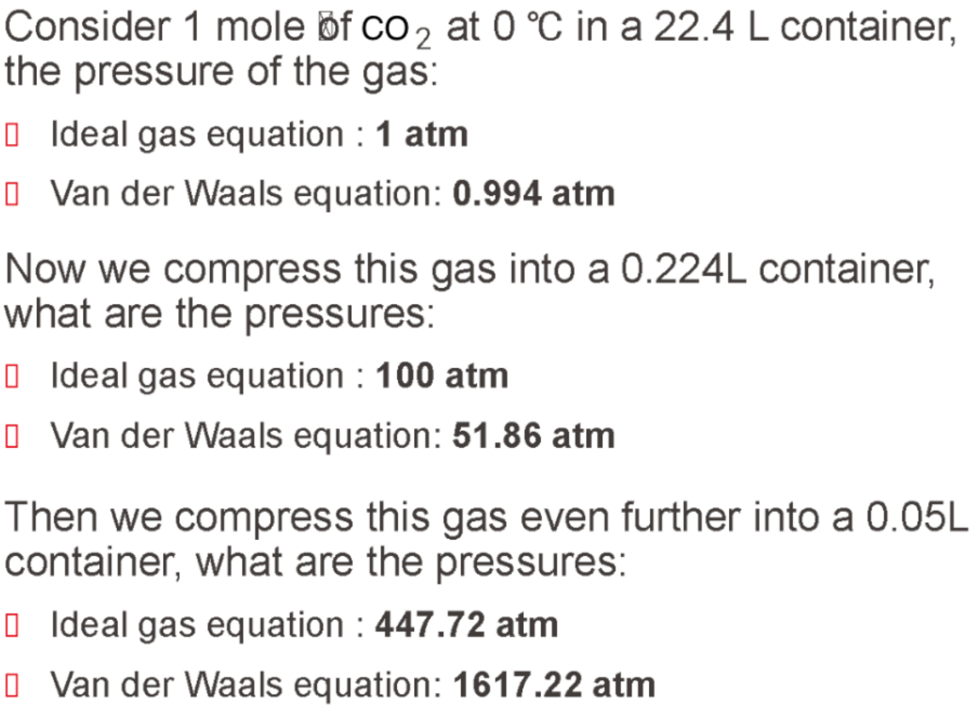
*(**b**) equal to the actual volume occupied by the molecules of 1 mol gas, with unit [L/mol]*

*(**a**) reflects how strong the gas molecules attract to each other, with unit [L^2-atm/mol^2]*

*Both **a** and **b** are gas dependent.*

Van der Waals equation: $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

Examples:



Consider 1 mole of CO_2 at 0 ℃ in a 22.4 L container, the pressure of the gas:

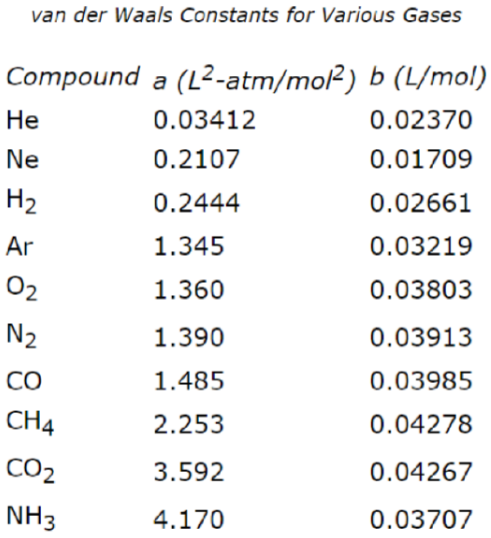
- Ideal gas equation : **1 atm**
- Van der Waals equation: **0.994 atm**

Now we compress this gas into a 0.224L container, what are the pressures:

- Ideal gas equation : **100 atm**
- Van der Waals equation: **51.86 atm**

Then we compress this gas even further into a 0.05L container, what are the pressures:

- Ideal gas equation : **447.72 atm**
- Van der Waals equation: **1617.22 atm**



van der Waals Constants for Various Gases

Compound	*a* (L^2-*atm/mol*^{2})	*b (L/mol)*
He	0.03412	0.02370
Ne	0.2107	0.01709
H_2	0.2444	0.02661
Ar	1.345	0.03219
O_2	1.360	0.03803
N_2	1.390	0.03913
CO	1.485	0.03985
CH_4	2.253	0.04278
CO_2	3.592	0.04267
NH_3	4.170	0.03707