Lecture 1

04 September 2024 13:26

The Perfect Gas

N.B. : "perfect" means no interactions

"ideal" means all interactions are the same

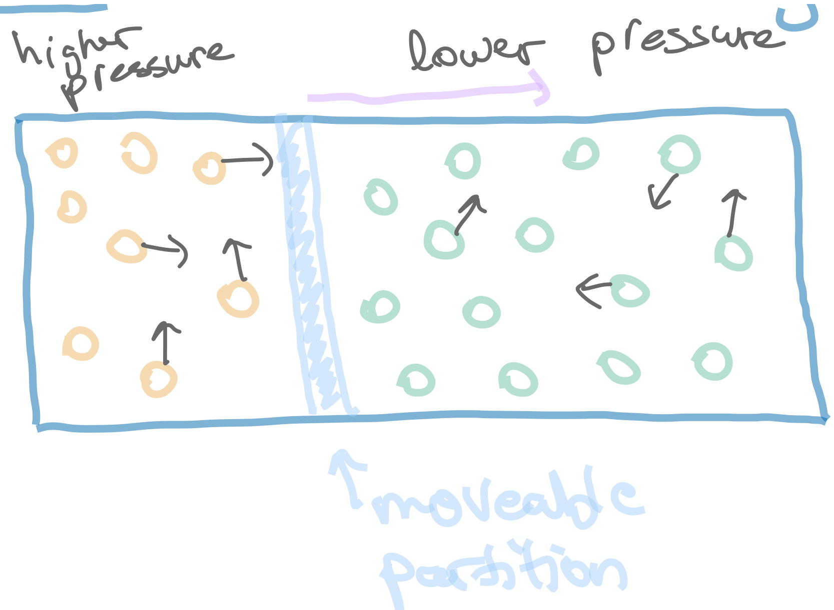
variables of state

What is a state ?

Let's suppose we have a system of three particles

① ② ③

Pressure : force divided by area



SI unit : pascal , Pa

$1\ Pa = 1\ N\ m^{-2} = 1\ kg\ m^{-1}\ s^{-2}$

$p^{\ominus} = 1\ bar$ ← standard state

<u>Volume</u> : the measure of the extent of space a gas occupies

SI unit : m^3

<u>Temperature</u> : related to the motion of molecules

Kelvin scale : absolute scale ; K

Amount : a measure of "how much"

a chemical species is present

$N_A = 6.022 \times 10^{23}\ mol^{-1}$

Intensive vs. extensive properties

Intensive ↑ does not depend on amount

extensive ↑ depends on amount

e.g. T

e.g. V

molar quantities : $X_m = \frac{X}{n}$

e.g. $V_m = \frac{V}{n}$

Equation of State

$p = f(T, V, n)$ ← where we want to end up

Empirical Laws

Boyle's Law : $pV =$ constant

(n, T constant)

Charles's Law : $V = \text{constant} \cdot T$

(n, p constant)

$p = \text{constant} \cdot T$

(n, V constant)

Avogadro's Principle : $V = \text{constant} \cdot n$

(p, T constant)

Combining these laws, we obtain

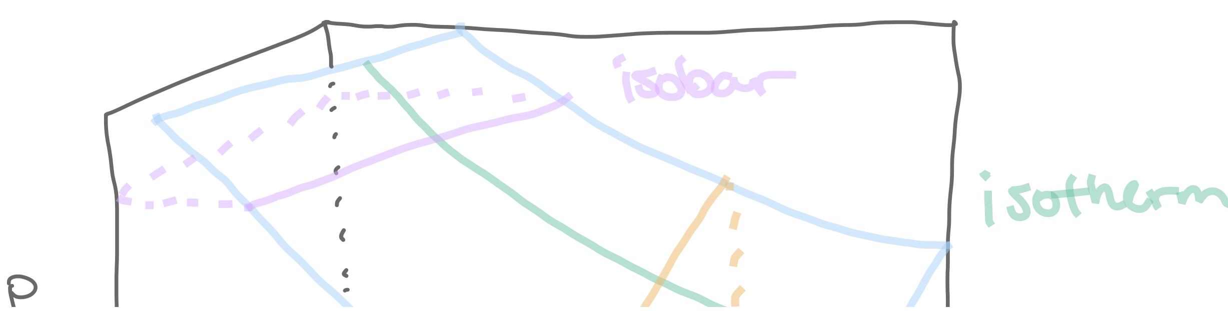
$$pV = \text{constant} \cdot nT$$

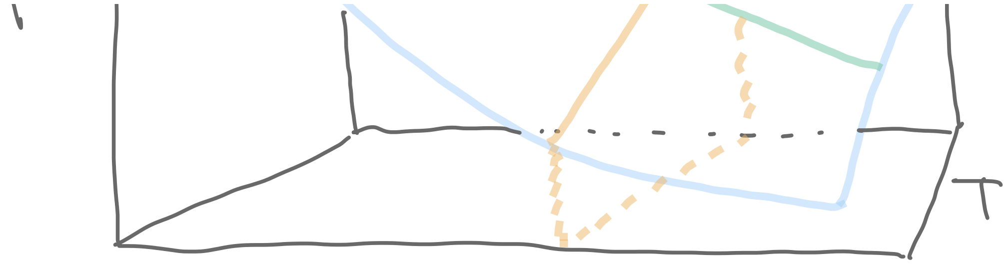
↑ gas constant

$$\boxed{pV = nRT}$$

perfect gas law, perfect gas equation of state

$$R = k_B \cdot N_A$$





Mixtures of Gases

partial pressure : $p_J = x_J p$

↑ mole fraction of component J

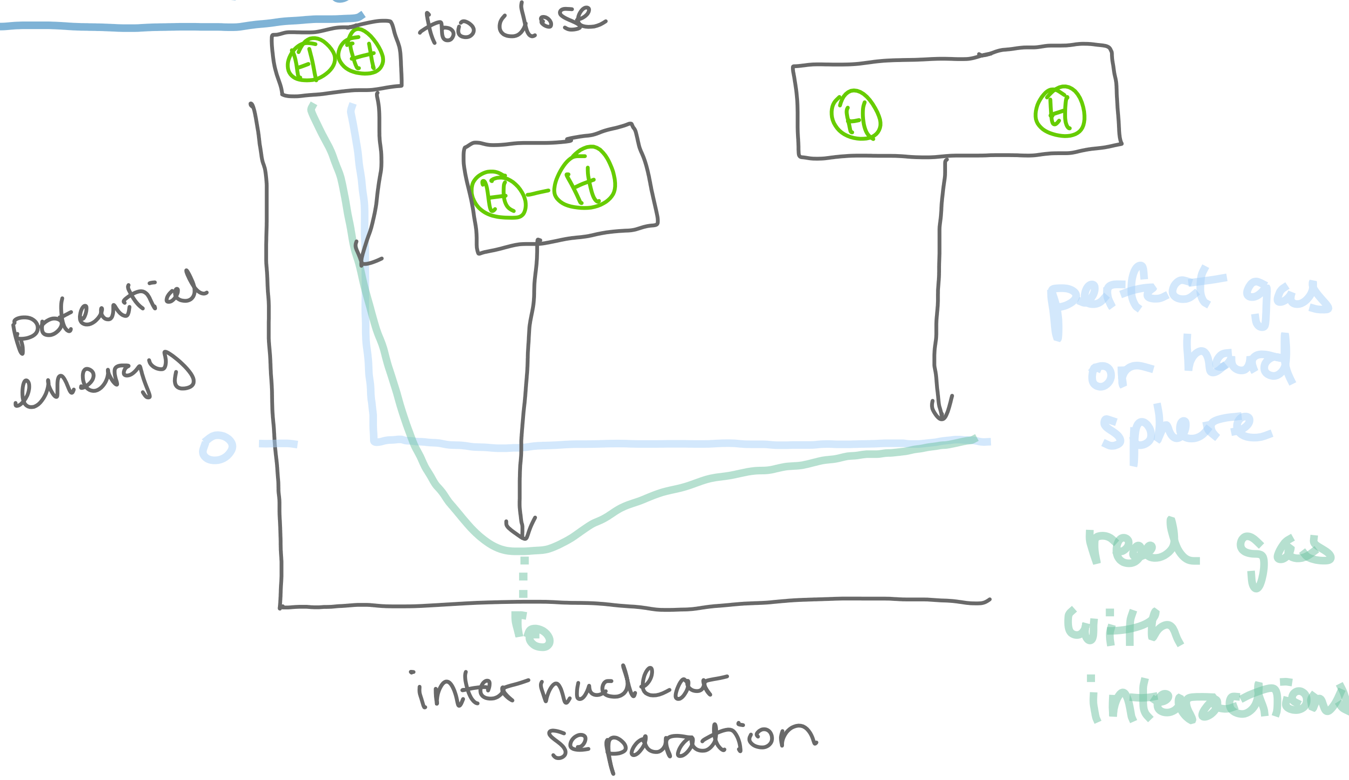
$$x_J = \frac{n_J}{n}, \quad n = n_A + n_B + \cdots$$

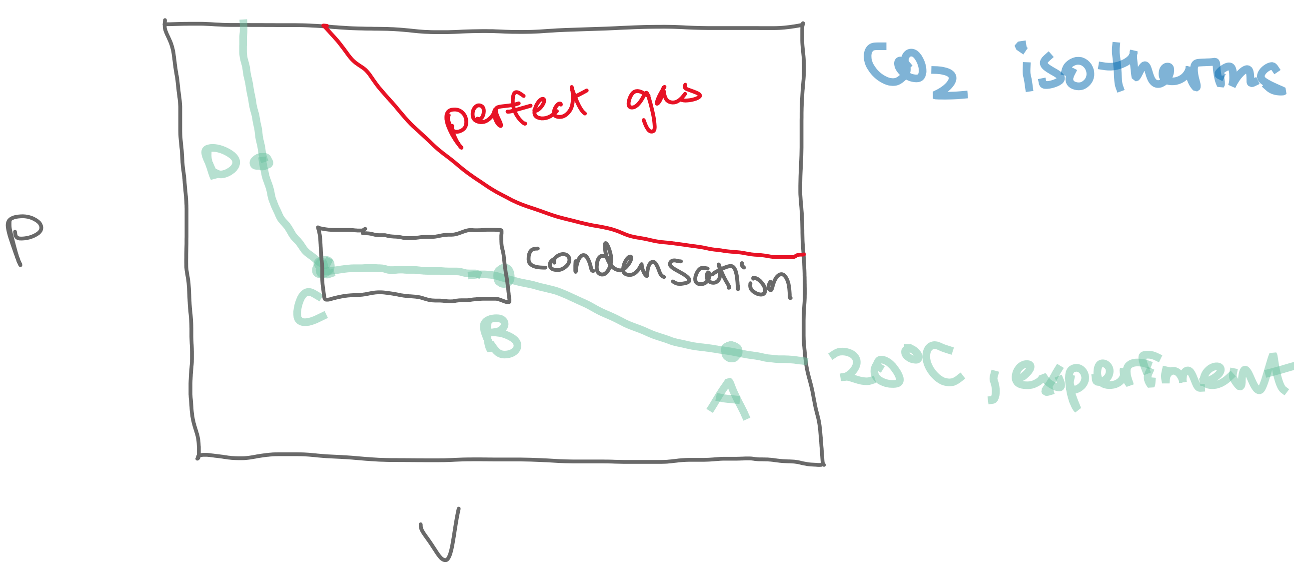
$$p_A + p_B + \cdots = (x_A + x_B + \cdots)p = p$$

(sum of all mole fractions = 1)

Dalton's Law : the pressure exerted by a mixture of gases is the sum of the pressures that each one would exert if it occupied the container alone. (perfect gases only)

Real Gases



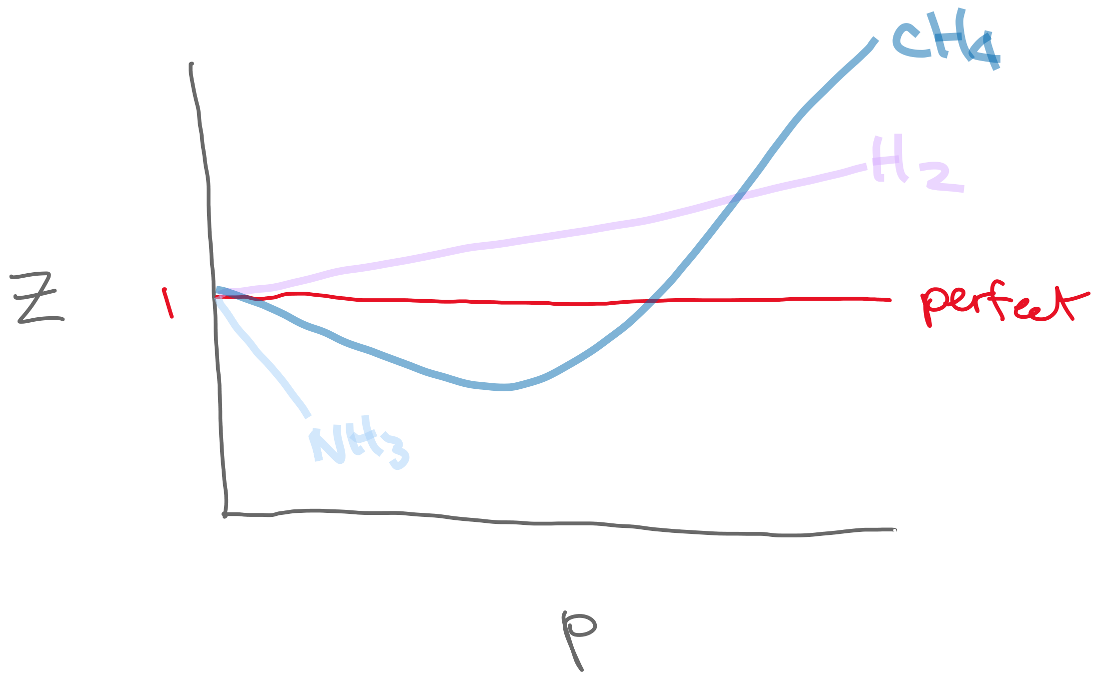


Compression Factor

$$Z = \frac{V_m}{V_m^\circ} \qquad V_m^\circ = \frac{RT}{p}$$

$$Z = \frac{V_m}{RT/p} = \frac{pV_m}{RT}$$

$$\boxed{pV_m = RTZ}$$



How do we describe real gases more quantitatively?

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

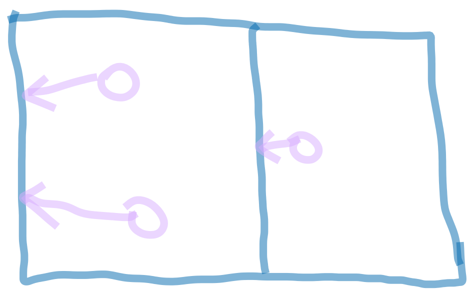
$$V_{excluded} = \frac{4}{3}\pi(2r)^3$$

$$p = \frac{nRT}{V-nb}$$

repulsive part

$$V_{excluded} = 8\,V_{molecule}$$

per molecule: $4\,V_{molecule}$



before after

attractive part reduces both the frequency of collisions as well as the force of each collision

$$p = \frac{nRT}{V-nb} - a\frac{n^2}{V^2}$$

van der Waals equation of state

$$p = \frac{RT}{V_m-b} - \frac{a}{V_m^2}$$

alternate form

(a, b are arbitrary parameters)