Lecture 1

Thursday, September 7, 2023 11:26

Topic 1A The Perfect Gas

Variables of state

Pressure, p, and volume, V

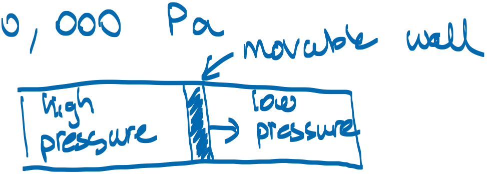
Pressure - defined as force F per area A

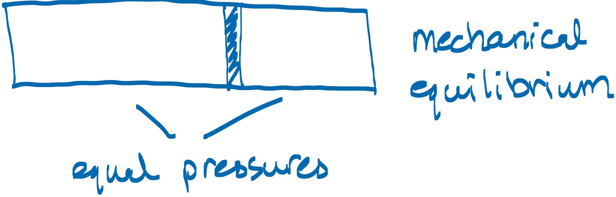
SI unit of pressure is the pascal Pa; $1 \text{ Pa} = 1 \text{ N m}^{-2}$

$F = ma$ $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

p° : standard pressure used to report physical quantities

- defined to be 1 bar or 100,000 Pa


movable wall
high pressure
low pressure


mechanical equilibrium
equal pressures

Volume V is a measure of the extent of the region of space a gas occupies ; SI unit : m^3

Temperature

- formally, a property that determines in which direction energy will flow *as heat* when two samples are in thermal contact.

T denotes the thermodynamic temperature

$T = 0$ as the lowest point ; absolute scale

$$T\,(K) = \theta\,({}^{\circ}C) + 273.15$$

Amount

Amount of substance, n, is a measure of the number of specified *entities* present in the sample

entities : may be atoms, molecules, or formula units

SI unit : mole (mol)

$1 \text{ mol} = 6.02214076 \times 10^{23}$ entities

Avogadro's constant, N_A

~~incorrect : number~~ of moles

$\boxed{\text{correct : amount in moles}}$

$$n = \frac{m}{M}$$

↖ molar mass

SI unit of M : kg mol^{-1}

but more convenient to use $\text{g} \cdot \text{mol}^{-1}$

Intensive and Extensive Properties

- suppose a sample is divided into smaller samples

extensive : the values of subsamples add up to those of the original sample i.e. depends on how much substance is present (e.g. V)

intensive: the values of subsamples remain the same as in the original; i.e. does *not* depend on how much substance is present (e.g. T)

molar value of property X: X_m

$$X_m = \frac{X}{n} \qquad V_m = \frac{V}{n}$$

$$\mu = \frac{G}{n}$$

$$G_m = \frac{G}{n}$$

Equations of State

Specify the state of a pure substance by giving the values of n, V, p, and T

In practice, we only need to specify three variables

$$p = f(T, V, n)$$

$$\boxed{p = \frac{nRT}{V} \qquad \text{perfect gas equation}}$$

Boyle's Law: $pV = \text{constant}$

at constant n, T

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

at constant n, p

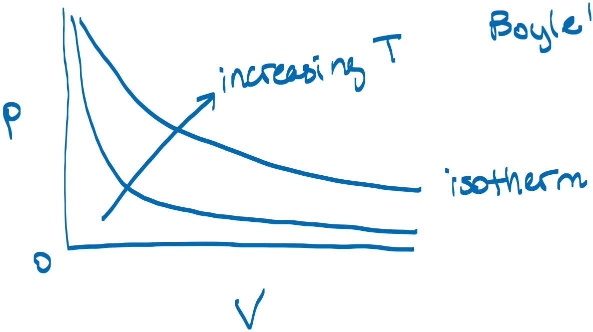
$p = \text{constant} \times T$

at constant n, V

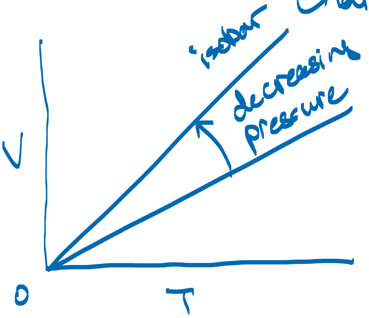
Avogadro's Principle: $V = \text{constant} \times n$

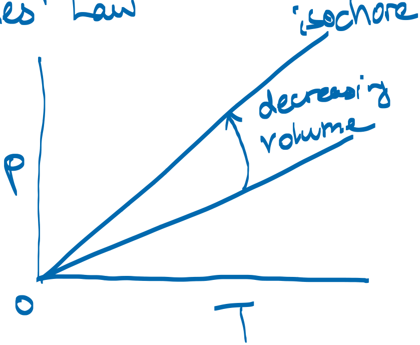
at constant p, T

Boyle's Law



Charles' Law





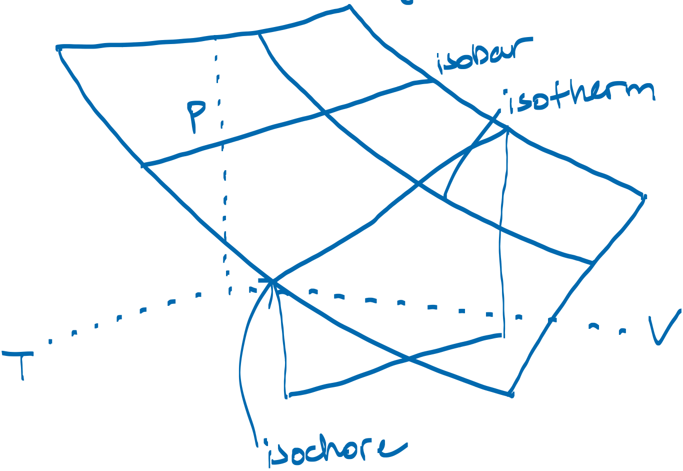
$$\boxed{pV = nRT}$$

perfect gas equation of state

perfect : all intermolecular interactions are the same, and are all zero

ideal : all intermolecular interactions

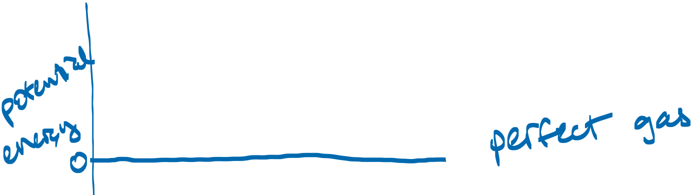
are the same only.

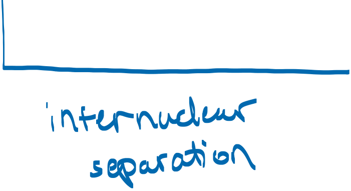

isobar
isotherm
p
T
V
isochore

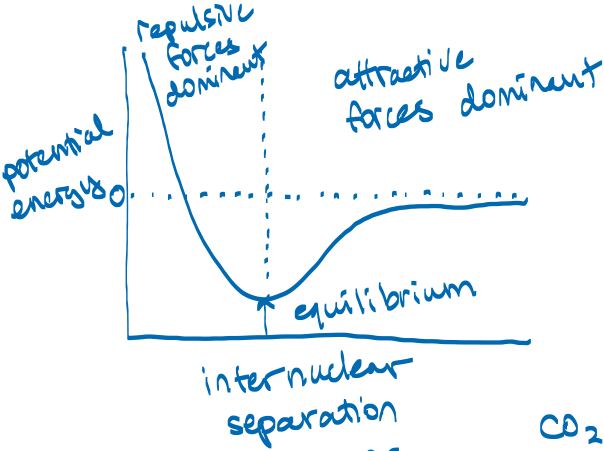
Topic 1C Real Gases

Real gases do not obey the perfect gas law except in the limit of $p \to 0$.

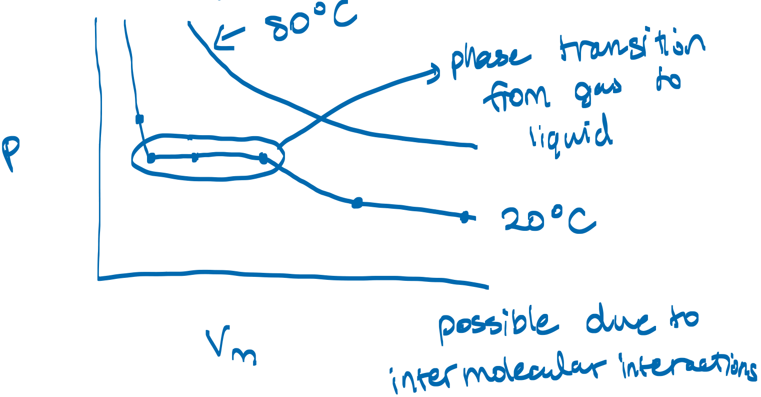
Deviations are strong at high p and low T.




internuclear separation


repulsive forces dominant
attractive forces dominant
potential energy
0
equilibrium
internuclear separation

CO_2


80°C
phase transition from gas to liquid
P
20°C
V_m
possible due to intermolecular interactions

Virial Coefficients

$$pV_m = RT$$

$$pV_m = RT(1 + B'p + C'p^2 + \dots)$$

virial expansion

The van der Waals equation

Repulsive interaction: suppose the molecules are hard spheres. Thus, instead of moving in volume V, they move in volume $\boxed{V - nb}$.

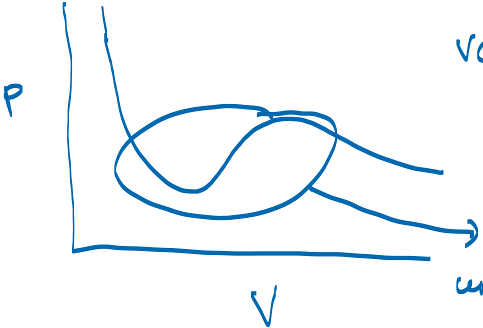
Attractive interaction: the frequency of collisions and strength of collisions are reduced by attractive forces.

$$\boxed{-a\frac{n^2}{V^2}}$$

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

van der Waals equation of state

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



vdW EoS

→ vdW loops unphysical