State properties

state property:
determines the macroscopic state of a physical system

state properties of single component gases:
amount of matter, pressure, volume, temperature $n$, $p$, $V$, $T$

amount of matter
- denoted by $n$
- name of the unit: mole (denoted by mol)
- 1 mol matter contains $N_A = 6.022 \cdot 10^{23}$ particles, Avogadro constant

pressure
- definition $p = F/A$,
- (force $F$ acting perpendicularly on area $A$)
- SI unit pascal (denoted by Pa): 1 Pa = 1 N m$^{-2}$
- 1 bar = $10^5$ Pa; 1 atm = 760 Hg mm = 760 torr = 101325 Pa
State properties 2

state properties of single component gases: \( n, p, V, T \)

**volume**  
denoted by \( V \), SI unit: \( \text{m}^3 \)  
volume of one mole matter \( V_m \)  
molar volume

**temperature**  
characterizes the thermal state of a body

many features of a matter depend on their thermal state:  
\textit{e.g.} volume of a liquid, colour of a metal

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**Temperature scales 1: Fahrenheit**

**Fahrenheit scale (1709):**

0 \(^\circ\)F   (-17.77 °C) the coldest temperature measured in the winter of 1709

100 \(^\circ\)F   (37.77 °C) temperature measured in the rectum of Fahrenheit’s cow between these temperatures the scale is linear (measured by an alcohol thermometer)

Problem: Fahrenheit personally had to make copies from his original thermometer

lower and upper reference temperature arbitrary

lower and upper reference temperature not reproducible

an „original“ thermometer was needed for making further copies
Temperature scales 2: Celsius

Centigrade scale or Celsius scale (1742; 1750):

0 °C temperature of melting ice in 1 atm air
100 °C temperature of boiling water in 1 atm air

Between these temperatures the scale is linear
(measured by an alcohol thermometer)

Problem: if other liquids are used (e.g. Hg),
then different middle temperatures are measured

Lower and upper reference temperature arbitrary
Lower and upper reference temperature reproducible
Anyone can make a new centigrade scale thermometer

Temperature scales 3: Kelvin

Kelvin scale or absolute temperature scale (1848):

0 K (-273.15 °C) extrapolated zero volume of an ideal gas
273.16 K (0.01 °C) temperature of the triple point of water

Between these temperatures the scale is linear
(measured by a gas thermometer)

Problem: ideal gas does not exist

Lower and upper reference temperatures physically well based
Lower and upper reference temperatures reproducible

This is the real („thermodynamic“) temperature scale
Zeroth Law of Thermodynamics

If substance A is in thermal equilibrium with substance B and
substance B is in thermal equilibrium with substance C
then substance A is in thermal equilibrium with substance C.

Note: the condition is thermal equilibrium, not
thermodynamic equilibrium!

What does it mean:
Using thermometer B, the temperature of body A,
then the temperature of body C is measured.
If the thermometer shows the same reading,
then the temperature of bodies A and C are equal.

Equation of state of the ideal gas: ideal gas law

\[ p \, V = n \, R \, T \quad \text{or} \quad p \, V_m = R \, T \]

\( p \) pressure (Pa)
\( V \) volume (m\(^3\))
\( n \) amount of matter (mol)
\( T \) temperature (K)
\( R \) gas constant \( R = 8.314 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} \)

“Regnault constant”

Henri Victor Regnault
(1810-1878)
French chemist

at high temperature and not very high pressure
the equation of state of the ideal gas is a good approximation.

DEF: ideal gas or perfect gas: imagined gas that obeys
exactly the perfect gas equation of state.
72 names on the Eiffel tower

http://en.wikipedia.org/wiki/List_of_the_72_names_on_the_Eiffel_Tower

Dalton’s Law

**DEF** For mixtures of gases, **partial pressure** of a component gas is the pressure exerted by this gas occupying the same volume alone.

**Dalton’s Law:** the pressure of a mixture of perfect gases is equal to the sum of the partial pressures.

\[
pV = (n_1 + n_2 + \ldots + n_k)RT
\]

\[
p = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \ldots + \frac{n_kRT}{V} = p_1 + p_2 + \ldots + p_k
\]

\[
x_j = \frac{n_j}{n_1 + n_2 + \ldots + n_k} = \frac{p_j}{p} = \frac{pV / RT}{pV / RT} = \frac{p_j}{p}
\]

⇒ mole fraction \( n_j \) of component \( j \) is the ratio of the corresponding partial pressure and of the total pressure.

John Dalton
(1766-1844)
English chemist
Real gases

DEF Imperfection of real gases can be characterized by the compression factor $Z$

$$Z = \frac{pV_m}{RT}$$

compression factor vs. pressure diagram of nitrogen gas
the significant effects are above 10 bar!

Compression diagram

DEF Compression diagram: $Z$ – $p$ curve

please note:
- at (almost) zero pressure $Z = 1$
- for an ideal gas $Z = 1$ always
- real gas, high pressure: high $Z$
- at the Boyle temperature: $Z$ starts horizontally
- below the Boyle temperature: $Z$ starts below 1
- above the Boyle temperature: $Z$ is always above 1

DEF: Boyle temperature: $Z(p)$ starts horizontally at this temperature

significance: at the Boyle temperature the real gases behave (almost) like the ideal gases if the pressure is not very high (e.g. $p < 30$ bar)
Boyle temperature for $N_2$: 54,05 °C (→ air behaves like an ideal gas at 298K)

shape of the $Z(p)$ curve:
curvature downwards: attracting forces between the molecules
going up: repelling forces / own volume of the molecules
Equations of state of real gases

TV virial equation of state \[ Z = \frac{pV_m}{RT} = 1 + B'p + C'p^2 + \ldots \]

please note:

using the virial equation of state, the \( Z(p) \) curve is approximated with a polynomial
the constant term is 1, because if \( p=0 \) then \( Z=1 \)

polynomial of any order can be used
→ any accuracy can be achieved

\( B', C', \ldots \) temperature dependent empirical constants
the favourite of chemical engineers due to its high accuracy

Robert Boyle (1627-1691)
English chemist

Equations of state of real gases 2

van der Waals equation of state

\[
\left( p + \frac{n^2a}{V^2} \right) (V - nb) = nRT
\]

the idea of van der Waals:

let us take the equation of state of ideal gases:

\[ pV = nRT \]

\( p \) pressure is corrected with a term that takes into account the attractive forces between the molecules. This term includes empirical constant \( a \).
\( V \) (the volume of the box) is corrected by the own volume of the molecules.
This volume is \( b \) for 1 mole, \( nb \) for \( n \) moles of molecules
\( a \) and \( b \) are empirical constants and do not depend on temperature

Johannes Diderik van der Waals (1837-1923)
Dutch physicist

This equation of state is simple, but not very accurate (say, error is below 1%).
**Isotherms of ideal gases**

**DEF**: 
Isotherms of gases: \( p(V) \) curve at constant temperature (axis \( x \): volume, axis \( y \): pressure)

lower temperature:  
the isotherm is getting closer to the axes, but keeping the hyperbolic shape  
(since \( p \cdot V = \text{constant} \) always)

**Isotherms of real gases**

high temperature:  
nearly hyperbolic (nearly ideal gas)  
lower temperature:  
distorted hyperbolic function  

**critical isotherm**: a point having horizontal tangent appears (**critical point**)
**critical temperature**: temperature of the critical isotherm
**critical pressure**: pressure belonging to the critical point  
**critical molar volume**: molar volume belonging to of the critical point

**significance of the critical temperature**: if the temperature is higher, the gas cannot be liquefied by compression
Isotherms of real gases 2

measured isotherms of CO$_2$

critical temperature: 304.3 K (31.1 °C)
critical pressure: 7.38 MPa (73.8 bar)

above the critical temperature: gas
below the critical temperature: vapour (liquefaction via compression)
grey area: vapour and liquid are in equilibrium at the vapour pressure

left of the gray area and below critical temperature: liquid

THE END
of topic
ideal gas and real gases