The properties of gases.
Ideal and real gases.

Lecture Outline:

I. An ideal gas and the ideal gas law. Changes of state: isothermal, isobaric and isochoric processes.

II. Mixtures of ideal gases, the concept of molar fractions, partial pressure, Dalton's law.

III. Description of real gases (isotherms). Compressibility. The van der Waals equation of state. The critical state.

IV. The interpretation of the pressure of a gas in the kinetic molecular theory of gases. Molecular justification of the pressure and volume correcting factors.

V. Speed distribution function. Energy distribution function. Collision of particles with the wall and with each other. Collision frequency. Collision numbers. Free mean path.

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Properties of gases (overview)

State of matter:	GAS (g)	LIQUID (l)	SOLID (s)
Fixed shape	no	no	yes
Fixed volume	no	yes	yes

An example of phenomenological description.

State of matter:	GAS (g)	LIQUID (l)	SOLID (s)
The particles' potential energy	small	medium	large
kinetic energy	large	medium	small
ordering	no	yes?	yes

An example of (qualitative) interpretation.

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Properties:

▪ **Pressure, p** – experience, c

Unknown Pressure
P

Fluid of interest
(Gas in most cases)

h

Vacuum

Glass tube

760 mm
(29.92 in)

Atmospheric pressure

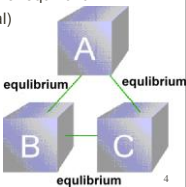Gage Pressure ΔP = P - P₀   Mercury

I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Properties:

▪ **Temperature, T** – experience (cold, hot).
  ▪ intensive property!
  ▪ units: °C, K, °F (USA)
  ▪ measurement: gas, liquid, resistance thermometers, *etc.*
  ▪ homogeneity (thermal conduction): thermal equilibrium
  ▪ wall: insulating or conducting (diathermal)

Zeroth law of thermodynamics

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

This is fundamental for measuring temperature.

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Properties:

▪ **Volume, V** – close to obvious
  ▪ extensive property!
  ▪ units: dm^3, liter
  ▪ measurement

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Properties:

▪ **Amount of substance (mole), n**
  ▪ extensive quantity!
  ▪ units:
    ▪ name: mole; symbol: mol (mmol, μmol)
    ▪ N_A = 6,022×10^{23} atoms, molecules, ions, e^-, ... The Avogadro constant is huge!
    ▪ fundamental property in SI (m, kg, s, A, K, cd)

▪ **Not the same as mass (kilogram in SI)!**

▪ **Avogadro's law:** at identical *p, V* and *T, different* gases contain the same number of particles.

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state:

- Phenomenological description.
- Quantitative connections between pairs of properties.
  - One possibility: determining the connection between p and V, measurement, plotting, setting up an equation:
    - $p \sim 1/V$ or ($V \sim 1/p$), that is $pV = $ constant
    - curve: isotherm [T = constant]
    - shape: hyperbolic
    - **Boyle's law (also Mariotte)**
    - limiting law: valid at small pressure and/or high temperature!

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state:

- Phenomenological description.
- Quantitative connection between pairs of properties.
  - Nonlinear equations are often linearized with a suitable mathematical transformation (in modern science, this is unnecessary and statistically undesirable).
    - Calculation of reciprocals is sufficient:
    - $p = f(1/V)$

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state: pV = constant

Boyle's law
constant temperature (isotherm)

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state: V/T = constant

Gay-Lussac's first (Charles') law
constant pressure (isobaric)

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state: p/T = constant

Gay-Lussac's second law
constant volume (isochoric)

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state:

- V (extensive) also depends on the amount of substance n
  (p and T do not, they are extensive):
  - V = constant × n (*i.e. V/n = constant*)
  - $V_m = V/n$; V_m = molar volume

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state:

- The three (or four?) laws unified:
  - $pV = nRT$ or $pV_m = RT$
- This is
  - **ideal gas law** (*alias*)
  - **ideal gas equation of state**.
- The concept **ideal gas** is in essence a **state** and not a particular substance (He and H_2 are not ideal gases themselves; at **low pressure and high temperature all gases behave like an ideal gas**.)

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I. Ideal gas and ideal gas law.
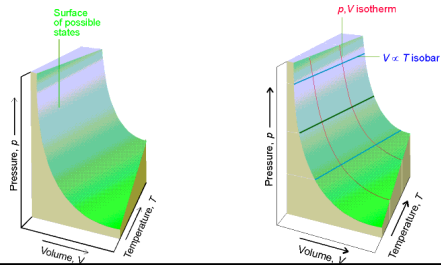### Changes of state: isothermal, isobaric, isochoric.

Changes of state:

- The three-variable equation of state requires a coordinate system in three dimensions (spatial).
  - Result: **surface of possible states** (all the allowed states [combinations of *p*, *T*, *V* values)
  - In essence a collection of an infinite number of isotherms, isobars and isochores

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state:

- The three-variable equation of state requires a coordinate system in three dimensions (spatial).

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I. Ideal gas and ideal gas law.
Changes of state: isothermal, isobaric, isochoric.

Changes of state:

- *Note*: in the phenomenological description, only the values of physical properties are considered. The energy changes accompanying the changes of states are not investigated.
- For example, there is no information on
  - the heat necessary for increasing the temperature of the gas or the heat evolved during cooling of a gas sample,
  - the work necessary to compress the gas or the work done by the gas upon expansion.

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II. Mixtures of ideal gases, the concept of molar fraction, partial pressure, Dalton's law.

Mixtures of gases: (multicomponent systems)

- Gases are fully miscible (air, natural gas, gas mixtures in industrial processes).
- Ideal gases form ideal mixtures.
  (The g-l, g-s, l-s, l-l, s-s mixtures are often non-ideal!)
- The phenomenological description is still sufficient, knowledge of the structure is unnecessary, there is no need to interpret the findings.
- **Law of combining gas volumes** (Gay-Lussac): needs interpretation, which contributed to the development of the particle-based (atom, molecule) theory of matter.

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II. Mixtures of ideal gases, the concept of molar fraction, partial pressure, Dalton's law.

Mixtures of gases: (multicompo

- **Dalton's law**: the pressure of a gases is the sum of the partial
  - $p = p_A + p_B + ...$
  - **partial pressure**: the pressure that component alone would exert und
    $p_j = n_j RT/V$ or $p_j = x_j p$
    (Partial molar properties will be discussed
  - **molar fraction**: the amount of subs component divided by the overall a
  - $x_j = n_j / n$,   where $n = n_A + n_B + ...$
  - possible values of x_j: $0 < x_j < 1$.
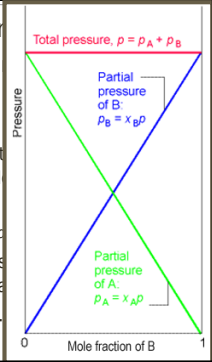
III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

Changes of state (real gases):

- *General experience:* the simple equations describing ideal gases are not valid under certain conditions (large p, small T), the isotherm gets distorted, the line is not hyperbolic any more, the equation $pV_m = RT$ does not hold.)
- *[Observation first, then precise description, finally explanations (may) follow!]*

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III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.
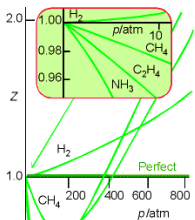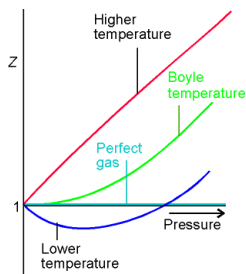
Changes of state (real gases):

- *General observation: $pV_m \neq RT$*
- *Solution:*
  - Demonstrate the deviation (numerically), and show its extent (e.g. on a linearized plot).
    - Ideal gas: $pV_m = RT$, so $pV_m/RT = 1$
    - **Real gas**: $pV_m/RT \neq 1$, so define $pV_m/RT = Z$
    - Z: **compression factor** (because the deviations always show up at high compressions)
  - Plot Z as a function of pressure: sometimes larger, sometimes smaller, if $p \to 0$, then $Z \to 1$.
  - *The deviation is demonstrated without a description.* 20

III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

Changes of state :

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III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

Changes of state: equations of state for real gases

- *Concept:* do not seek a new equation, keep the fundamentals of the $pV_m = RT$ form but modify it.
- A mathematical method using Virial coefficients, which yields the **Virial equation of state**:
  - $pV_m = RT(1 + B'p + C'p^2 + \ldots)$ or
  - $pV_m = RT(1 + B/V_m + C/V_m^2 + \ldots)$
- This modification makes it possible to describe the experimental data precisely, but the values of B, C, ... must be measured for every gas at every T!
- Assessment: the form of the equation is the same, the constant can b measured precisely, but they depend on T and the identity of the gas. 22

III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

Changes of state: equations of state for real gases

- *Concept:* do not seek a new equation, keep the fundamentals of the $pV_m = RT$ form but modify it.
- Another method: the **van der Waals equation** (there are several similar others, but this is the most common)
- Didactic form (the corrections of *p* and *V* shown):

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

- Assessment: the two correction constant (*a* and *b*) depend on the identity of the gas, but they are independent of *T* and *p* in a large range (there is no need to measure and record a lot of values). **Simplicity!**
- The values of the constants can be interpreted based on the molecular properties of the gas. **Beauty!** 23
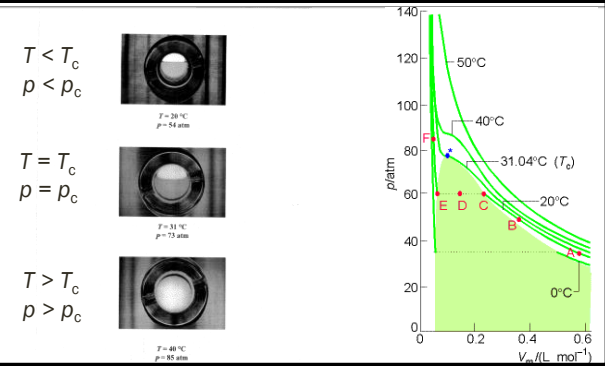
III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

Continue the ideal gas → real gas li

- The *p-V* isotherms get more dis then a state is reached at whic interface appears or disappea
- This is the **critical state**, and th the isotherm, which is mathem inflexion.
- The critical point is characteriz
  - T_c: critical temperature
  - p_c: critical pressure
  - V_c: critical molar volume
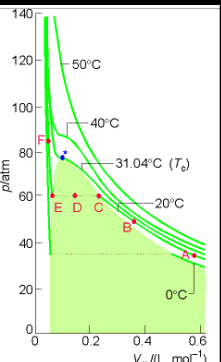
III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

$T < T_c$
$p < p_c$

$T = T_c$
$p = p_c$

$T > T_c$
$p > p_c$

III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

Surfaces of states:

ideal gas

p,V isotherm

$V \propto T$ isobar

real gas

1.5
1.0
0.8
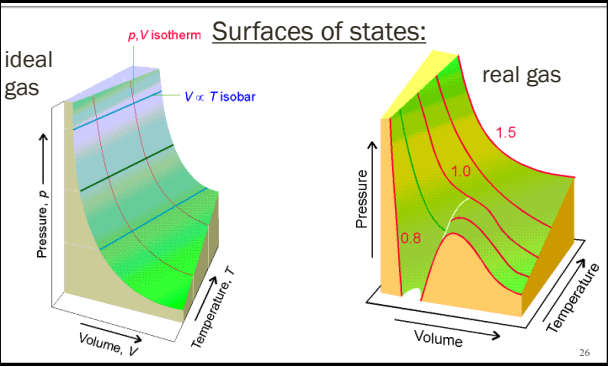
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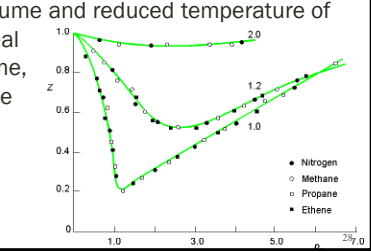
Relation between critical properties and van der Waals constants a and b (still phenomenological):

- The first and second derivatives with respect to V_m are 0:

  - $$\frac{dp}{dV_m} = 0 \quad \text{and} \quad \frac{d^2p}{dV_m^2} = 0$$

- Consequently:
  - $V_c = 3b$ $p_c = a / 27b^2$ $T_c = 8a / 27Rb$
    (critical properties)
  - $Z_c = p_c V_c / RT_c = 3/8$
    (critical compression factor)

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III. Description of real gases (isotherms). Compression factor. The van der Waals equation of state. The critical state.

The principle of corresponding states:

- Dimensionless reduced variables:
  - $p_r = p/p_c$ $V_r = V_m/V_c$ $T_r = T/T_c$
- If the reduced volume and reduced temperature of two samples of real gases are the same, then they exert the same reduced pressure.

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

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Practical applications of gas laws

- description of the atmosphere (+barometric formula)
- gas thermometers (for scientific purposes)
- liquefaction of gases
- transport and storage of (natural) gas
- technology of gas phase reaction (synthesis of HCl, NH$_3$, pyrolysis, organic syntheses *etc*.)
- high pressure instrumentation, processes (pneumatic devices, compressors, explosions)
- vacuum technology for generating reduced pressures

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IV. Interpretation of gas pressure in the kinetic molecular theory. Molecular justification of the pressure and volume correcting factors.

Ideal gas:

- molecules with mass m, and speed v
- momentum: mv and kinetic energy: $\frac{1}{2}mv^2$
- the size of the molecules is negligible compared to the mean free path (molecules are mass points)
- a single interaction: completely elastic collision (negligible attraction or repulsion).

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IV. Interpretation of gas pressure in the kinetic molecular theory. Molecular justification of the pressure and volume correcting factors.

Ideal gas:

Interpretation of the pressure exerted on the wall: the colliding molecules change their momentum mv_x.

- Result:

$$pV_m = \frac{1}{3}Mc^2 \quad \text{or} \quad p = \frac{Mc^2}{3V_m}$$

where $M = N_A m$ (molar mass), $c = <v^2>^{1/2}$ root mean square speed (because kinetic energy is $\frac{1}{2}mv^2$).

On comparison with the $pV_m = RT$ ideal gas law:

- temperature T primarily reflects the (average) kinetic energy of the molecules:

$$T = \frac{Mc^2}{3R}$$

- $R = kN_A$, where k is the Boltzmann constant.
- The ideal gas law is thus interpreted or derived!

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IV. Interpretation of gas pressure in the kinetic molecular theory. Molecular justification of the pressure and volume correcting factors.

What about <u>real gases</u>?

- Molecules with mass m move ra~ collisions are not elastic.
- There is repulsion and attraction **p needs a correction**!
  - Pressure correction originates solely repulsive and attractive forces.
  - Instead of p, $(p + a/V_m^2)$ is used. a d the gas, but not on T.
- At high **p**, the size of the molecul relative to the free mean path, s
  - Volume corrections: proportional to t Instead of V_m, $(V_m - b)$ is used. b dep gas but not on T.
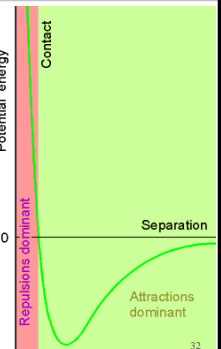
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IV. Interpretation of gas pressure in the kinetic molecular theory. Molecular justification of the pressure and volume correcting factors.

<u>van der Waals constants of a few gases</u>

Note: increasing polarizability and molecule size results in increasing correcting factors.

| Molecule	a (dm^6 bar mol^{-2})	b (cm^3 mol^{-1})
He	0.034598	23.733
H_2	0.24646	26.665
N_2	1.3661	38.577
O_2	1.382	31.86
C_6H_6 (benzene)	18.876	119.74

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V. Speed distribution function. Energy distribution function. Collision of particles with the wall and with each other..

Speed distribution functions:

- It would be possible for every molecule to have the same speed. But it is not so!
- Based on the kinetic theory of perfect gases, Maxwell found that the velocity of gas molecules has a well-defined "distribution„: this is called **Maxwell speed distribution**.

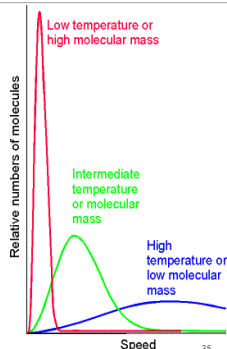$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$
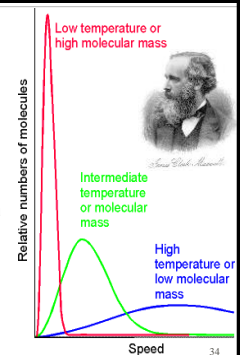
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V. Speed distribution function. Energy distribution function. Collision of particles with the wall and with each other.

Information content of the function (curve):

- starting point
- „endpoint"
- it has a maximum
- it is asymmetric
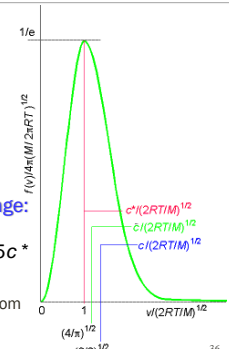- curve area (parts)
- effect of T
- effect of M

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V. Speed distribution function. Energy distribution function. Collision of particles with the wall and with each other.

Different <u>speeds</u>:

- Most probable speed:

$$c^* = \sqrt{\frac{2RT}{M}}$$

- Average speed:

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{4}{\pi}}c^* = 1{,}128c^*$$

- Square quadrant quadrangle average:

$$c = \langle v^2 \rangle^{1/2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3}{2}}c^* = 1{,}225c^*$$

Average speeds of gas molecules in the classroom are similar to the sound velocity (~ 300 m/s). *Understandable:* this makes the sound spread.

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V. Speed distribution function. Energy distribution function. Collision of particles with the wall and with each other.

Energy distribution functions:
- From statistical (probability) considerations, Boltzmann found that the one-dimensional velocity of the perfect gas molecules shows a definite "distribution" according to kinetic energy: this is called **Boltzmann energy distribution**.

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}$$

$$E_{kin,x} = \tfrac{1}{2} mv_x^2$$

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V. Speed distribution function. Energy distribution function. Collision of particles with the wall and with each other.

Energy distribution functions:
- Based on the Boltzmann energy distribution for one-dimensional moving motion, the energy distribution of the total kinetic energy of the perfect gas can also be given.
- These fisctions at different temperatures are similar to the sape of the Maxwell speed distribution function.

$$f(E) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT}\right)^{3/2} \sqrt{E} e^{-E/kT}$$

$$E = \tfrac{1}{2} mv^2$$
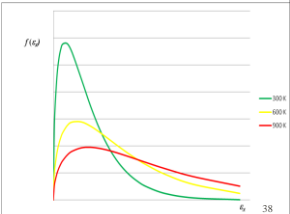
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Movies, animations
Boyle's law

The ideal gas law

Kinetic theory of gases

Speed distribution

Van der Waals gases

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