

# 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.

# Properties of gases (overview)

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

An example of phenomenological description.

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

An example of (qualitative) interpretation.

# I. Ideal gas and ideal gas law.

## Changes of state: isothermal, isobaric, isochoric.

### Properties:

- **Pressure,  $p$**  – experience, concept (force/area)
  - intensive property!
  - units: **Pa**, atm, Hgmm, (USA: PSI) *etc.*
  - measurement: barometers and manometers
  - fast propagation (pressure wave, explosions)
  - homogeneous in small spaces (diffusion) (vs. atmosphere)
  - wall of a container: movable or fixed; membrane

# I. Ideal gas and ideal gas law.

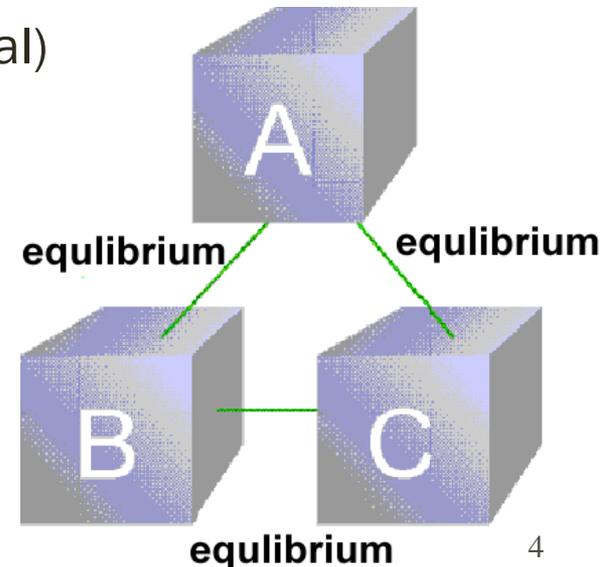
## Changes of state: isothermal, isobaric, isochoric.

### 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.

# I. Ideal gas and ideal gas law.

Changes of state: isothermal, isobaric, isochoric.

## Properties:

- **Volume,  $V$**  – close to obvious
  - extensive property!
  - units:  $\text{m}^3$ ,  $\text{dm}^3$ , liter
  - measurement

# 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**,  **$\mu$ mol**)
  - $N_A = 6,022 \times 10^{23}$  atoms, molecules, ions,  $e^-$ , ...  
The Avogadro constant is huge!
  - fundamental property in SI (m, kg, s, A, K, cd)
- **Avogadro's law**: at identical  $p$ ,  $V$  and  $T$ , *different* gases contain the same number of particles.

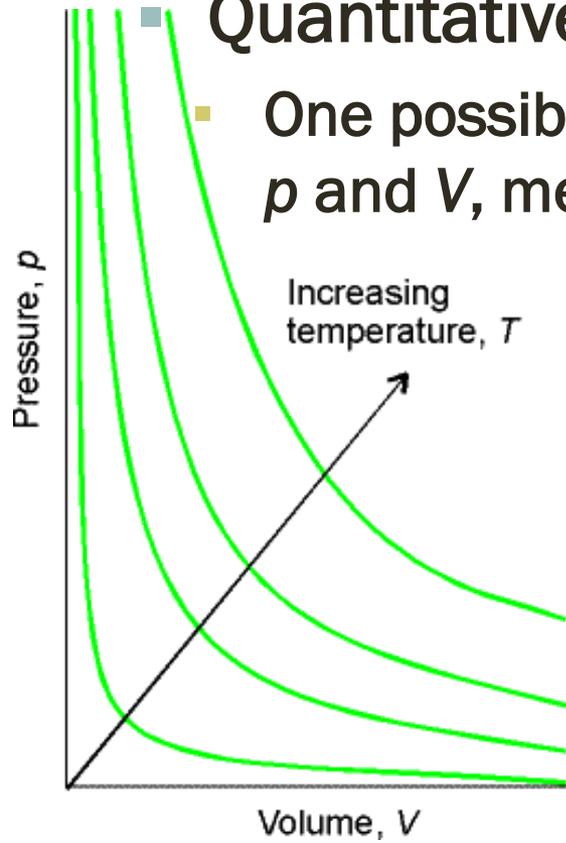


# I. Ideal gas and ideal gas law.

## 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  $pV = \text{constant}$
- curve: isotherm [ $T = \text{constant}$ ]
- shape: hyperbolic
- **Boyle's law (also Mariotte)**
- limiting law: valid at small pressure and/or high temperature!

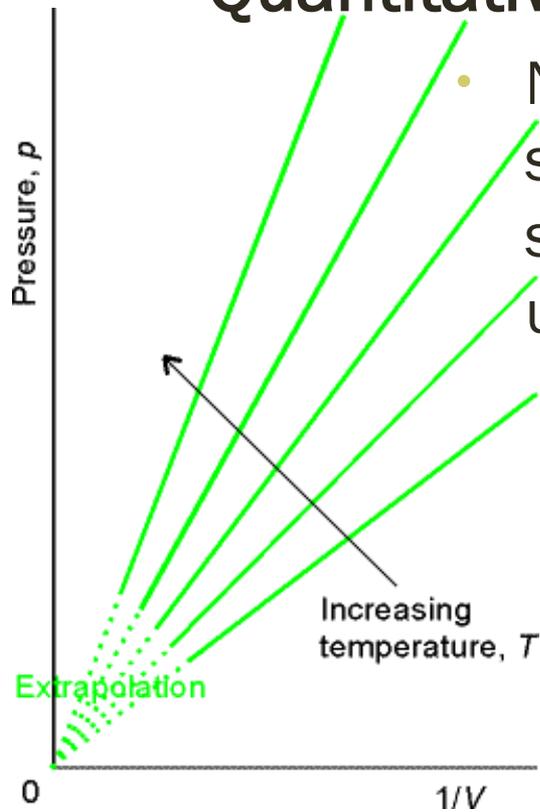
# I. Ideal gas and ideal gas law.

Changes of state: isothermal, isobaric, isochoric.

## Changes of state:

- Phenomenological description.
- Quantitative connection between pairs of properties.

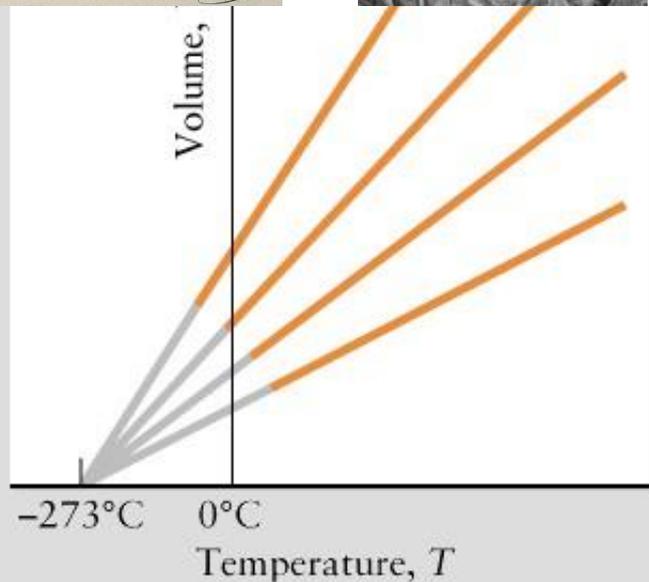
- Nonlinear equations are often linearized with a suitable mathematical transformation (in modern science, this is unnecessary and statistically undesirable).



# I. Ideal gas and ideal gas law.

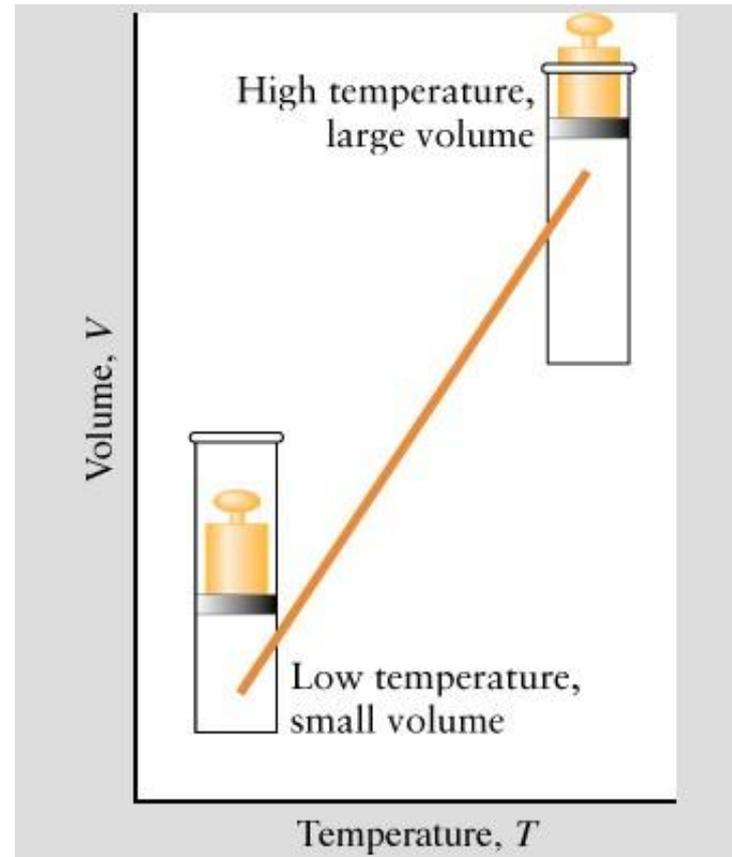
Changes of state: isothermal, isobaric, isochoric.

## Changes of state:



$$V/T = \text{constant}$$

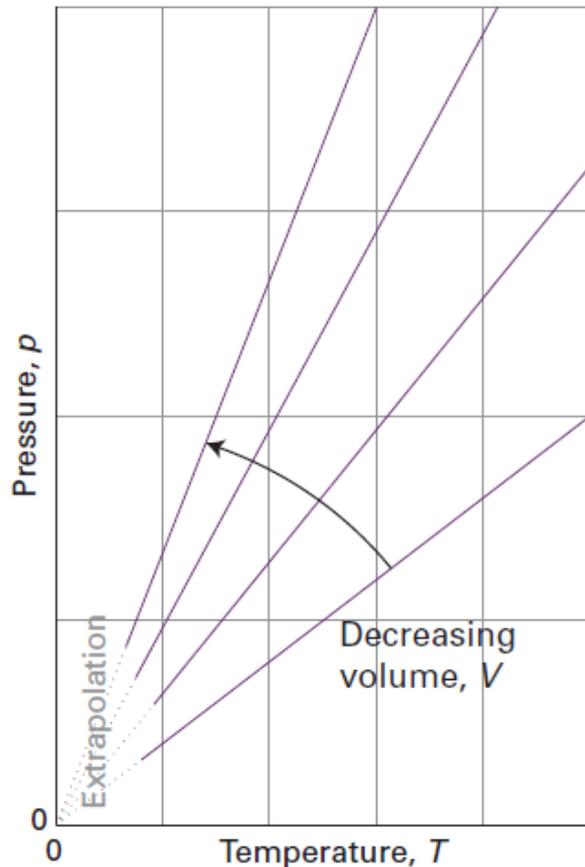
Gay-Lussac's first (Charles') law  
constant pressure (isobaric)



# I. Ideal gas and ideal gas law.

## Changes of state: isothermal, isobaric, isochoric.

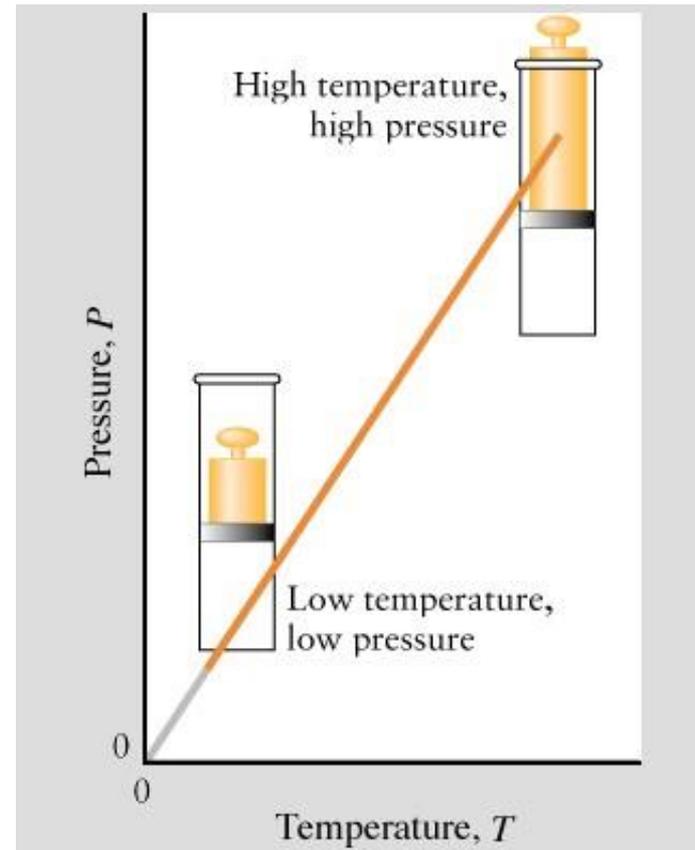
### Changes of state:



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

Gay-Lussac's second law

constant volume (isochoric)



# 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 intensive):
  - $V = \text{constant} \times n$  (i.e.  $V/n = \text{constant}$ )
  - $V_m = V/n$ ;  $V_m = \text{molar volume}$

# I. Ideal gas and ideal gas law.

Changes of state: isothermal, isobaric, isochoric.

## Changes of state:

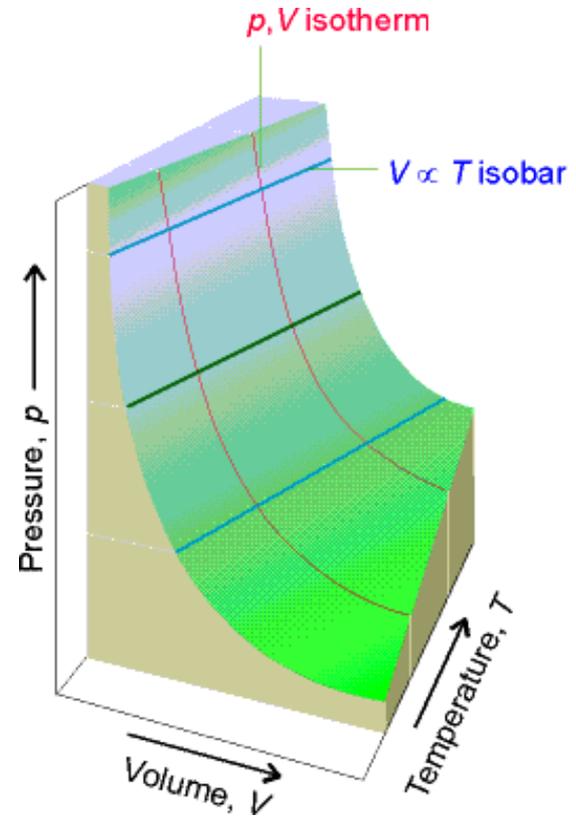
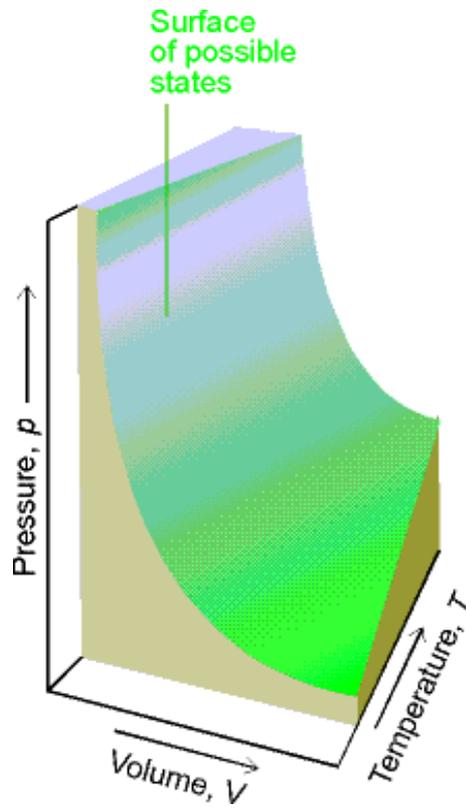
- The three (or four?) laws unified:
  - $pV = nRT$  or  $pV_m = RT$
- This is
  - **ideal gas law** (*alias*)
  - **ideal gas equation of state.**
- The concept **ideal gas** is in essence a **state** and not a particular substance (He and H<sub>2</sub> are not ideal gases themselves; at **low pressure and high temperature all gases behave like an ideal gas.**)

# 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).



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

### Mixtures of gases: (multicomponent systems)

- **Dalton's law:** the pressure of a mixture of ideal gases is the sum of the partial pressures:
  - $p = p_A + p_B + \dots$
  - **partial pressure:** the pressure that the selected component alone would exert under the same conditions:  
 $p_j = n_j RT/V$  or  $p_j = x_j p$   
*(Partial molar properties will be discussed later.)*
  - **molar fraction:** the amount of substance of the selected component divided by the overall amount of substance
  - $x_j = n_j/n$ , where  $n = n_A + n_B + \dots$
  - 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!]*

### III. Description of real gases (isotherms).

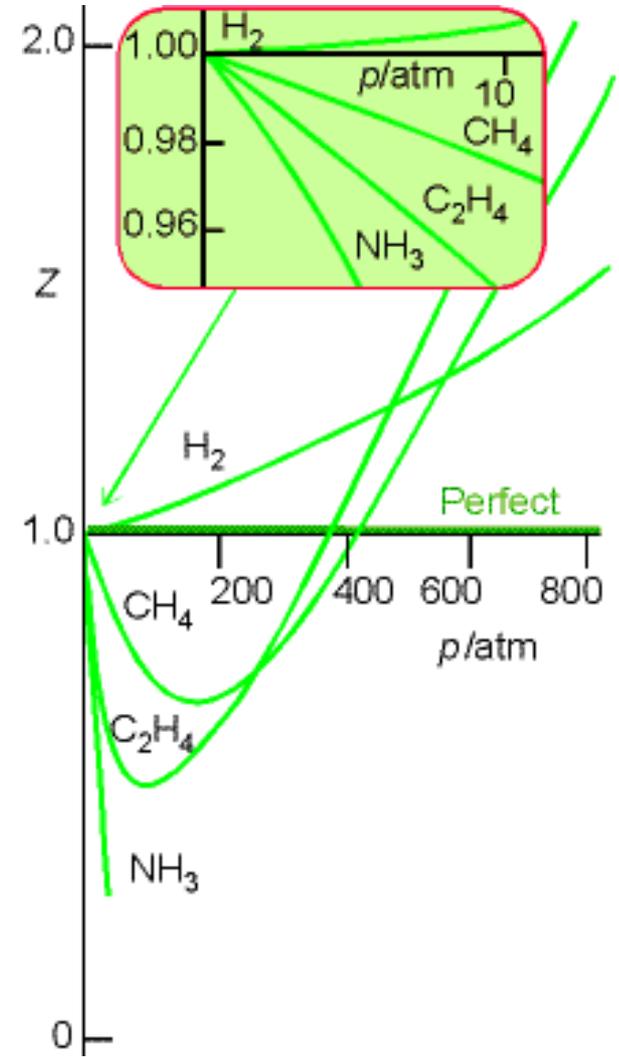
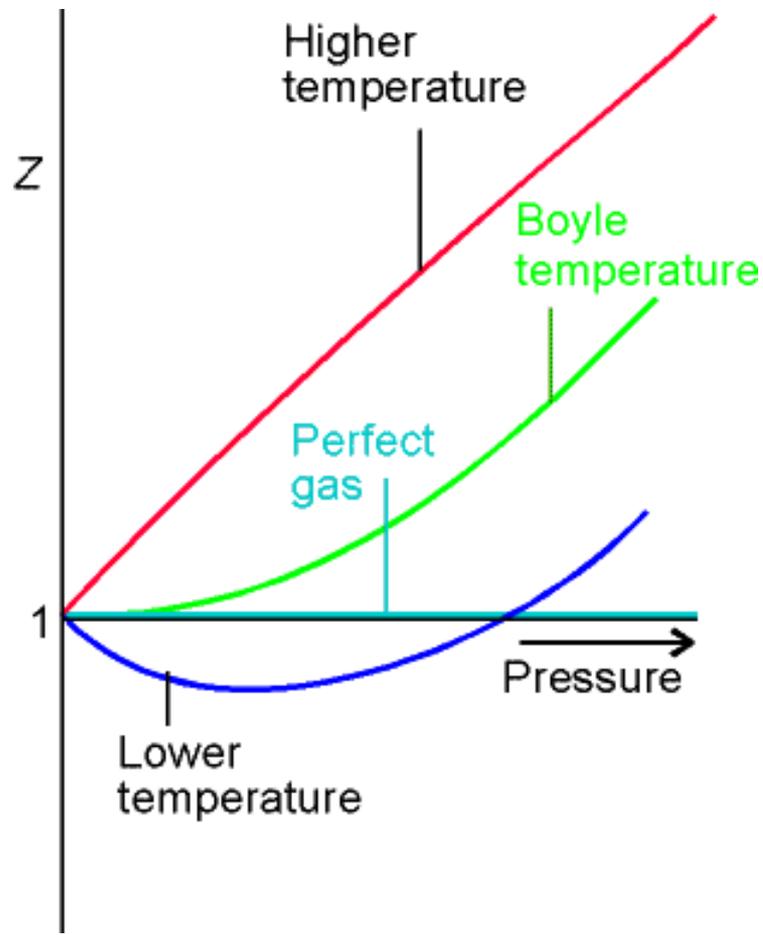
## Compression factor. The van der Waals equation of state. The critical state.

### 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  $p \rightarrow 0$ , then  $Z \rightarrow 1$ .
  - *The deviation is demonstrated without a description.*

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

## Changes of state :



### 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:**
  - $pV_m = RT(1 + B'p + C'p^2 + \dots)$  or
  - $pV_m = RT(1 + B/V_m + C/V_m^2 + \dots)$
- 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 be measured precisely, but they depend on  $T$  and the identity of the gas.

# 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!**

### III. Description of real gases (isotherms).

## Compression factor. The van der Waals equation of state. The critical state.

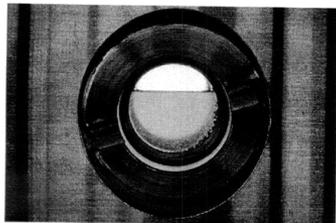
Continue the ideal gas  $\rightarrow$  real gas line of thought.

- The  $p$ - $V$  isotherms get more distorted at lower  $T$ , then a state is reached at which gas-liquid interface appears or disappears.
- This is the **critical state**, and the **critical point**, on the isotherm, which is mathematically a flat inflexion.
- The critical point is characterized by:
  - $T_c$ : critical temperature
  - $p_c$ : critical pressure
  - $V_c$ : critical molar volume

# III. Description of real gases (isotherms).

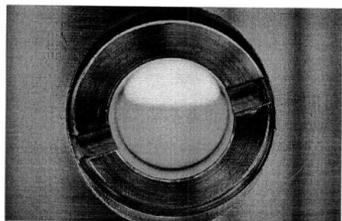
## Compression factor. The van der Waals equation of state. The critical state.

$$T < T_c$$
$$p < p_c$$



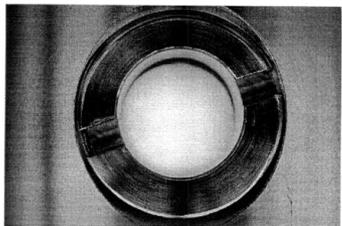
$T = 20\text{ °C}$   
 $p = 54\text{ atm}$

$$T = T_c$$
$$p = p_c$$

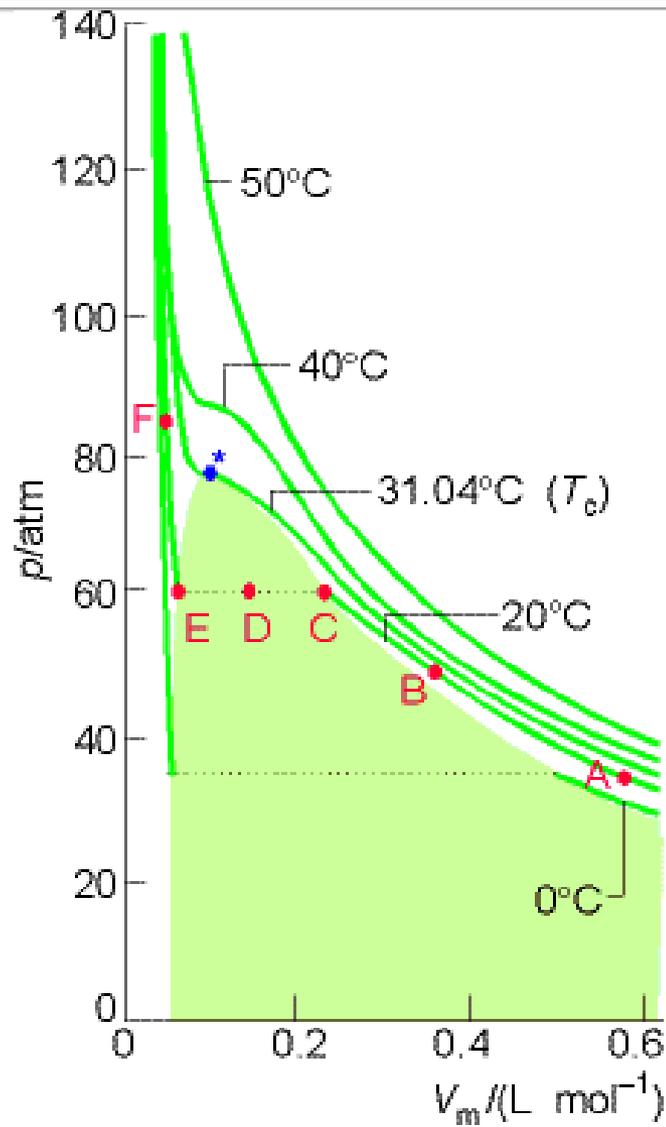


$T = 31\text{ °C}$   
 $p = 73\text{ atm}$

$$T > T_c$$
$$p > p_c$$



$T = 40\text{ °C}$   
 $p = 85\text{ atm}$



### III. Description of real gases (isotherms).

## Compression factor. The van der Waals equation of state. The critical state.

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:

- $$V_c = 3b \quad p_c = a / 27b^2 \quad T_c = 8a / 27Rb$$

(critical properties)

- $$Z_c = p_c V_c / RT_c = 3/8$$

(critical compression factor)

# III. Description of real gases (isotherms).

## Compression factor. The van der Waals equation of state. The critical state.

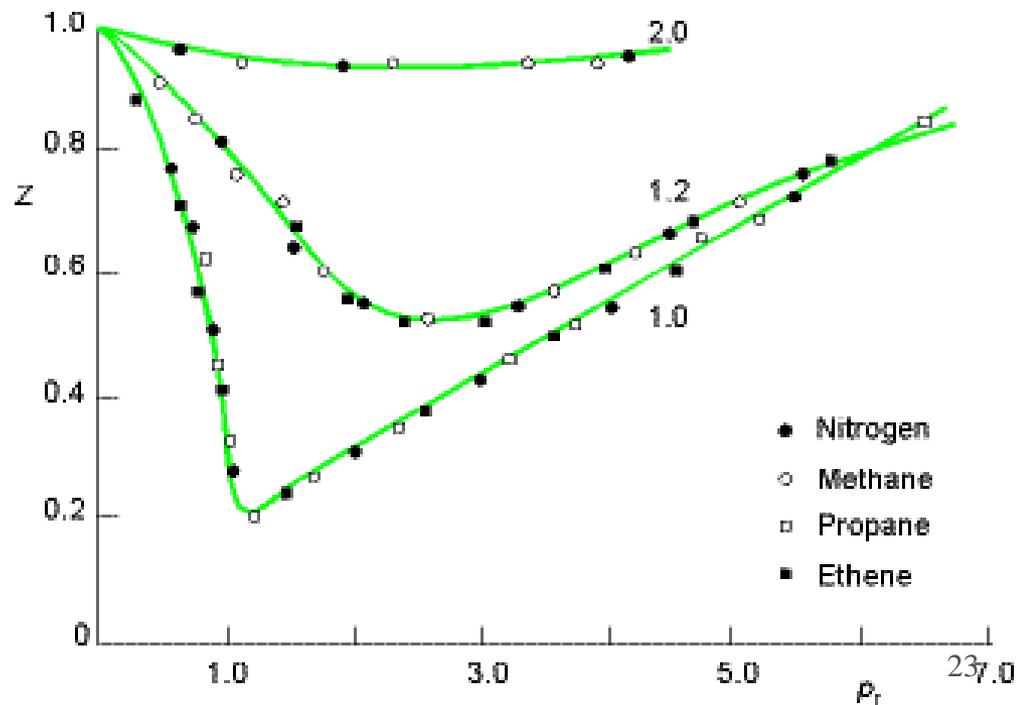
### The principle of corresponding states:

- 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.

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



# 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).

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

What about real gases?

- Molecules with mass  $m$  move randomly, but the collisions are not elastic.
- There is repulsion and attraction between molecules:  **$p$  needs a correction!**
  - Pressure correction originates solely from intermolecular repulsive and attractive forces.
  - Instead of  $p$ ,  $(p + a/V_m^2)$  is used.  $a$  depends on the identity of the gas, but not on  $T$ .
- At high  $p$ , the size of the molecules is not negligible relative to the free mean path, so  **$V$  needs a correction!**
  - Volume corrections: proportional to the volume of molecules. Instead of  $V_m$ ,  $(V_m - b)$  is used.  $b$  depends on the identity of the gas but not on  $T$ .

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

## van der Waals constants of a few gases

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

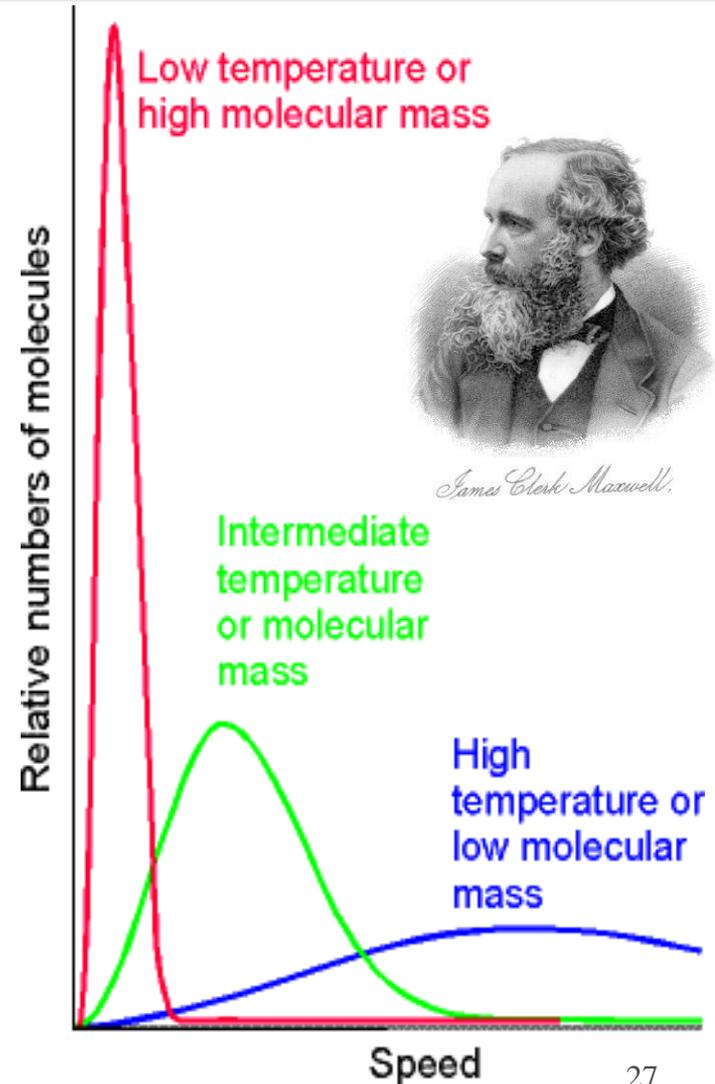
Molecule	$a$ ( $\text{dm}^6 \text{ bar mol}^{-2}$ )	$b$ ( $\text{cm}^3 \text{ mol}^{-1}$ )
He	0.034598	23.733
H <sub>2</sub>	0.24646	26.665
N <sub>2</sub>	1.3661	38.577
O <sub>2</sub>	1.382	31.86
C <sub>6</sub> H <sub>6</sub> (benzene)	18.876	119.74

# V. Speed distribution function. Energy distribution function.

## 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**.

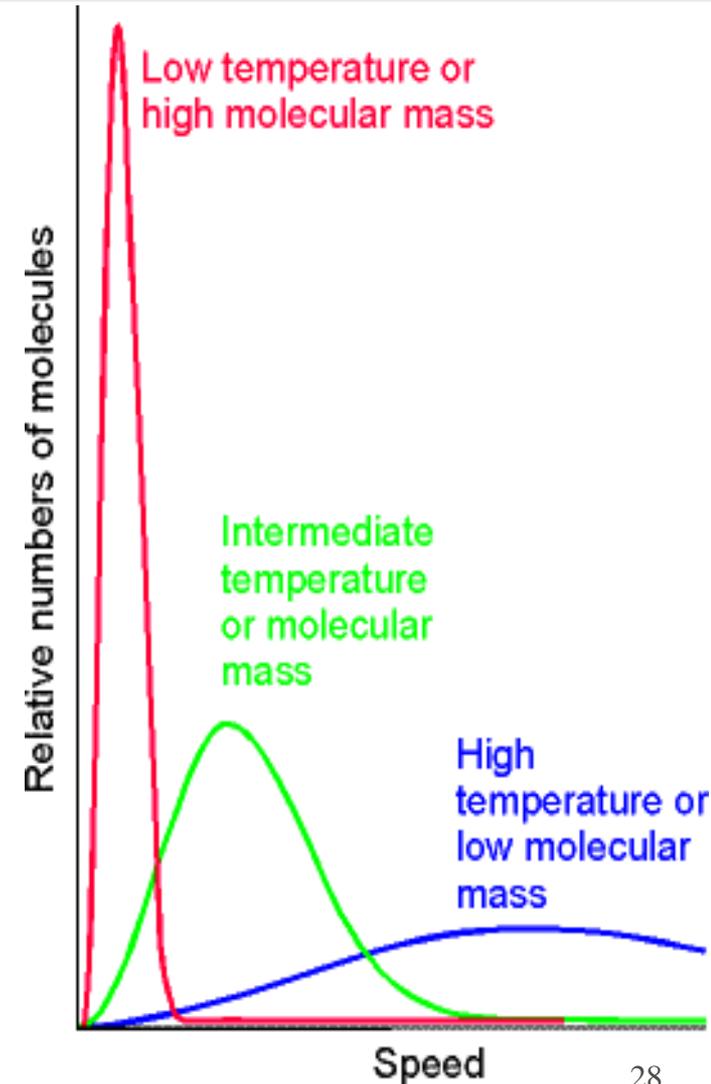
$$f(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2 / 2RT}$$



# V. Speed distribution function. Energy distribution function.

Information content of the function (curve):

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



# V. Speed distribution function. Energy distribution function.

Different speeds:

- Most probable speed:

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

- Average speed:

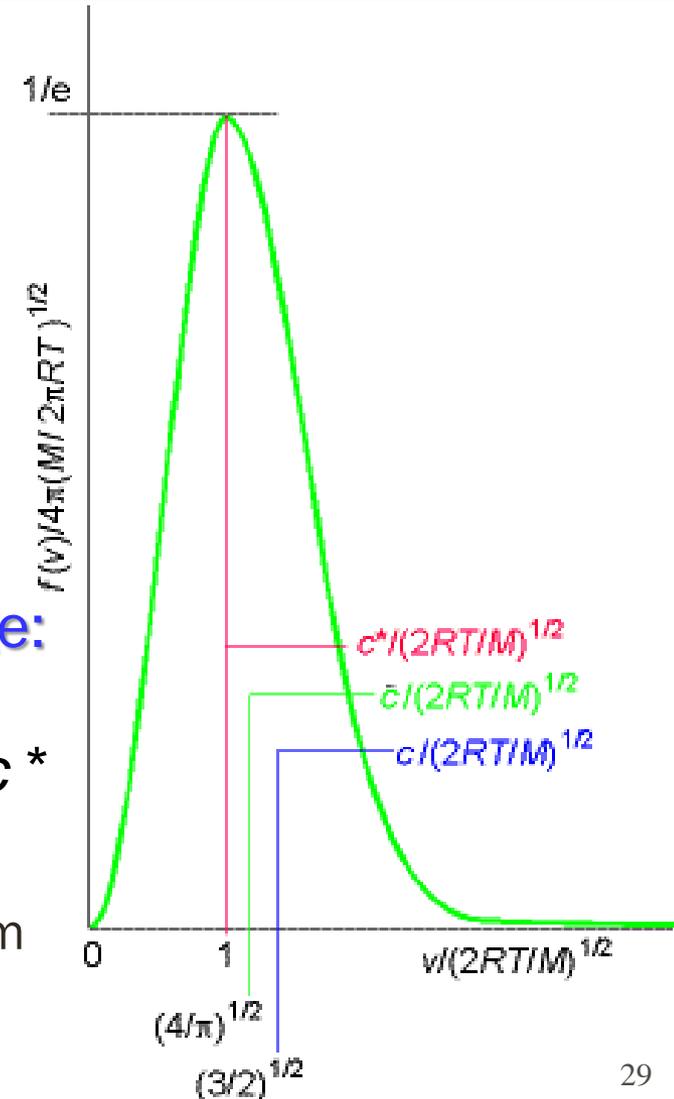
$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{4}{\pi}} c^* = 1,128 c^*$$

- Square quadrant quadrangle average:

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

Average speeds of gas molecules in the classroom are similar to the sound velocity ( $\sim 300$  m/s).

*Understandable*: this makes the sound spread.



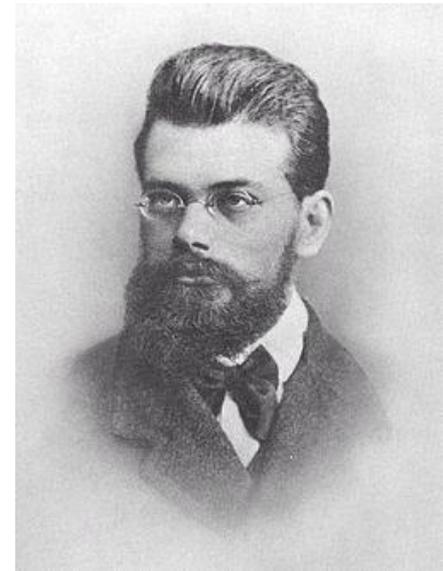
# V. Speed distribution function. Energy distribution function.

## 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.**

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

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



# V. Speed distribution function. Energy distribution function.

## 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 functions at different temperatures are similar to the shape of the Maxwell speed distribution function.

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

