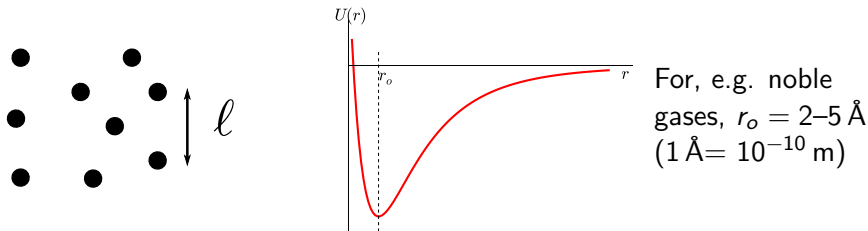


OVERVIEW

- Molecular theory of gases: Ideal gas equation
- Mixtures of ideal gases, humidity
- Heat capacities of ideal gas; Dulong and Petit law
- Equipartition of energy

MOLECULAR THEORY OF GASES



For N molecules of gas confined to a volume V , *concentration* $n = N/V$. The typical distance between molecules $\ell \sim n^{-1/3}$
For air at standard conditions $n \sim 3 \times 10^{25} \text{ m}^{-3}$, hence $\ell \sim 30 \text{ \AA}$

For gases at around room temperature and around atmospheric pressure

$$\ell \gg r_o$$

And neglecting the interactions is a good first approximation.

KINETIC-MOLECULAR MODEL OF AN IDEAL GAS

ASSUMPTIONS OF THE MODEL:

- 1 A container with volume V contains $N \gg 1$ identical molecules with mass m
- 2 Molecules act as point particles (i.e.: their size is much much smaller than the typical distance between them)
- 3 Molecules do not interact with each other
- 4 Molecules are in constant motion and occasionally collide with the container walls
- 5 Each collision is perfectly elastic

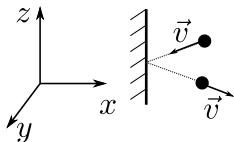
For simplicity, we also assume that the container walls are infinitely massive

IDEAL GAS PRESSURE

Consider a molecule colliding with the wall:

The change of momentum

$$dP_x = mv_x - (-mv_x)$$



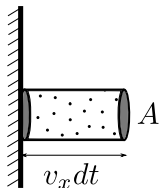
The force

$$F = \frac{dP_x}{dt} \times (\# \text{ of collisions})$$

Q: What is the number of molecules colliding with the wall during time dt ?

IDEAL GAS PRESSURE II

For simplicity assume that all the molecules have the same velocity (this is wrong, and we'll undo this assumption in a minute)



To collide with the wall during time dt , a molecule must be no further from the wall than $v_x dt$ — it must be within an imaginary cylinder of the volume $Av_x dt$.

The number of collisions per area A during time dt is then

$$(Av_x dt) \frac{N}{V} \times \underbrace{\frac{1}{2}}_{\text{left- and right-movers}}$$

IDEAL GAS PRESSURE III

Overall, the force is:

$$F = \frac{2mv_x}{dt} \times Av_x dt \frac{N}{V} \frac{1}{2} = mv_x^2 \frac{N}{V} \times A$$

and the pressure

$$p = F/A = mv_x^2 \frac{N}{V}$$

Can now undo the assumption that all molecules have the same velocity:

$$v_x^2 N = \underbrace{v_{x;1}^2 + v_{x;2}^2 + \cdots + v_{x;N}^2}_{N \text{ terms}} = N \langle v_x^2 \rangle$$

Where $\langle v_x^2 \rangle \equiv \frac{1}{N} (v_{x;1}^2 + v_{x;2}^2 + \cdots + v_{x;N}^2)$ is the *average* value of the v_x^2 .

IDEAL GAS PRESSURE IV

Since x-, y-, and z- directions are equivalent (effects due to gravity can be neglected)

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

and

$$\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = 3\langle v_x^2 \rangle$$

and finally

$$\begin{aligned} pV &= \frac{1}{3} m \langle v^2 \rangle N \\ &= \frac{2}{3} \underbrace{m \langle v^2 \rangle}_{2} N \end{aligned}$$

average kinetic energy of a molecule

IDEAL GAS PRESSURE V

$$pV = \frac{2}{3} \frac{m \langle v^2 \rangle}{2} N$$

compare to the ideal gas equation ($\nu = N/N_A$)

$$pV = \nu RT = \frac{N}{N_A} RT$$

Temperature is the measure of the average kinetic energy of the molecules of a gas

$$\frac{m \langle v^2 \rangle}{2} = \frac{3}{2} k_B T$$

Here

$$k_B = R/N_A = 1.38 \times 10^{-23} \text{ J/K}$$

is the so-called *Boltzmann constant*

EQUATIONS OF STATE: A MIXTURE OF IDEAL GASES

- Humid air: the mixture of air and water vapor
- the air itself is approximately 78% N_2 , 21% O_2 , and the rest (Ar, CO_2 etc) total $<1\%$.

For a mixture of ideal gases a, b, \dots , the *partial pressure* of a component is defined as the pressure the component would have had if the other components were not present:

$$p_a V = \nu_a RT, \quad p_b V = \nu_b RT, \quad \text{etc}$$

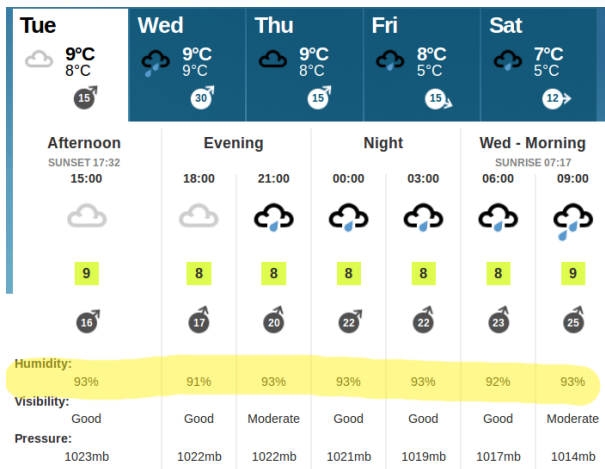
So that the net pressure is the sum of the *partial pressures*:

$$p = p_a + p_b + \dots, \text{ and}$$

$$\underbrace{(p_a + p_b + \dots)}_{\text{net pressure } p} V = \underbrace{(\nu_a + \nu_b + \dots)}_{\text{net number of moles } \nu} RT$$

HUMIDITY

`news.bbc.co.uk`/weather forecasts:



What exactly is *humidity*?

HUMIDITY (*relative* HUMIDITY, TO BE PRECISE)

Saturated vapor: a vapor phase of a substance when in equilibrium with the liquid (or solid) phase of the substance.

The pressure at which vapor saturates — *saturated vapor pressure* or just *vapor pressure* — depends on the temperature.

$$\text{Humidity} = \frac{\text{partial pressure of water vapor in the air}}{\text{saturated vapor pressure}}$$

When humidity = 100%, the air saturates [cf fog]

Dew point: (saturated) vapor pressure, $p_s(T)$, decreases as the temperature decreases. Cool the wet air: humidity increases until it reaches 100%. Cool the air further down \Rightarrow vapor condenses [until its pressure equals $p_s(T)$ again].

INTERNAL ENERGY OF A (MONOATOMIC) IDEAL GAS

Q: What is the average kinetic energy of a mole of an ideal gas?

A: For a single molecule,

$$\frac{m\langle v^2 \rangle}{2} = \frac{3}{2}k_B T \quad (\text{a single molecule})$$

Multiplying both sides by N_A , and noticing that $N_A m = \mu$ (the molar mass), and that $R = k_B N_A$, we obtain

$$\frac{\mu\langle v^2 \rangle}{2} = \frac{3}{2}RT \quad (\text{a mole of (monoatomic) ideal gas})$$

To be precise, we only considered *monoatomic* gases: we only took into account translational motion of molecules.

INTERNAL ENERGY OF A (MONOATOMIC) IDEAL GAS

Recall that the *internal energy* U is defined as

$$\begin{aligned} U &= \text{average kinetic energy of molecules} \\ &\quad + \text{potential energy of their interactions} \quad (= 0 \text{ for ideal gas}) \\ &= \frac{3}{2}\nu RT \end{aligned}$$

for ν moles of monoatomic ideal gas.

From the first law of thermodynamics: $U = \nu c_V T$ where c_V is the *molar isochoric heat capacity*, and $c_p = c_V + R$

$$c_V = \frac{3}{2}R \quad c_p = \frac{5}{2}R \quad (\text{monoatomic ideal gas})$$

HEAT CAPACITIES OF GASES

We have predicted:

$$c_V = \frac{3}{2}R = 1.5 \times 8.314 \text{ J/mol K} = 12.47 \text{ J/mol K}$$

Experimentally (at standard conditions):

| | Gas | c_V , J/mol K | c_V/R |
|------------|------------------|-----------------|---------|
| Monoatomic | He | 12.47 | 1.5 |
| | Ar | 12.47 | 1.5 |
| Diatomic | H ₂ | 20.42 | 2.46 |
| | N ₂ | 20.76 | 2.50 |
| | O ₂ | 20.85 | 2.51 |
| | CO | 20.85 | 2.51 |
| Polyatomic | CO ₂ | 28.46 | 3.42 |
| | SO ₂ | 31.39 | 3.78 |
| | H ₂ S | 25.95 | 3.12 |

THE NUMBER OF DEGREES OF FREEDOM

$$c_V = \frac{3}{2}R$$

The factor of **3** comes from the fact that our space is three-dimensional:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

Degrees of freedom:

The number of *degrees of freedom* (of an object) is the number of independent variables we need to describe its motion.



A diatomic molecule has two independent rotation axes \Rightarrow it has $3 + 2 = 5$ degrees of freedom.

A polyatomic molecule generally has *three* independent axes (our space is three-dimensional!)

EQUIPARTITION OF ENERGY

In thermal equilibrium, the average energy *per degree of freedom* is

$$\frac{1}{2}k_B T \quad (\text{per molecule})$$

$$\frac{1}{2}RT \quad (\text{per mole})$$

monoatomic molecules: $f = 3 \quad c_V = \frac{3}{2}R$

diatomic molecules: $f = 3 + 2 \quad c_V = \frac{5}{2}R$

polyatomic molecules: $f = 3 + 3 \quad c_V = \frac{6}{2}R$

(unless the molecule is linear)

HEAT CAPACITIES OF IDEAL GASES II

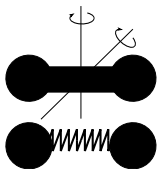
Experimentally (at standard conditions):

| | Gas | $c_V/R(\text{expt})$ | c_V/R (predicted) |
|------------|------------------|----------------------|---------------------|
| Monoatomic | He | 1.50 | 1.50 |
| | Ar | 1.50 | 1.50 |
| Diatomic | H ₂ | 2.46 | 2.50 |
| | N ₂ | 2.50 | 2.50 |
| | O ₂ | 2.51 | 2.50 |
| | CO | 2.51 | 2.50 |
| Polyatomic | CO ₂ | 3.42 | 3.0 |
| | SO ₂ | 3.78 | 3.0 |
| | H ₂ S | 3.12 | 3.0 |

Agreement with experiment is better, but there's still something else!

VIBRATIONAL DEGREES OF FREEDOM

Vibrational degrees of freedom:



Atoms in a molecule can oscillate around their equilibrium positions. A better model of a chemical bond is a spring connecting two atoms

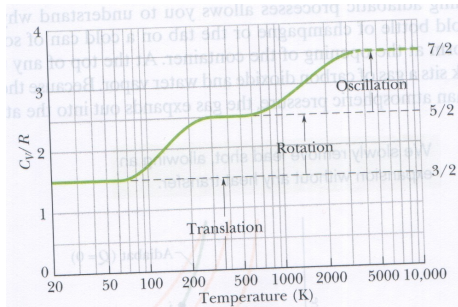
There are two vibrational degrees of freedom per bond

Two equivalent explanations:

- both atoms oscillate
- a spring has kinetic and potential energies

HEAT CAPACITIES OF GASES II

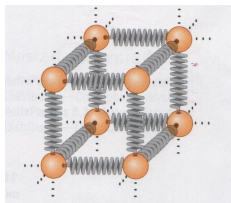
Experimental values of c_V for molecular hydrogen, H_2 :



Vibrational motion “freezes out” below certain temperatures (and so does rotational motion). This is a quantum mechanical effect.

HEAT CAPACITIES OF CRYSTALLINE SOLIDS

Consider a *monoelemental* solid.



A simplest model of a solid consists of balls connected by springs. Each spring has two degrees of freedom (or, each atom has kinetic and potential energy), hence equipartition of energy predicts for N atoms

$$U = 3k_B T \times N$$

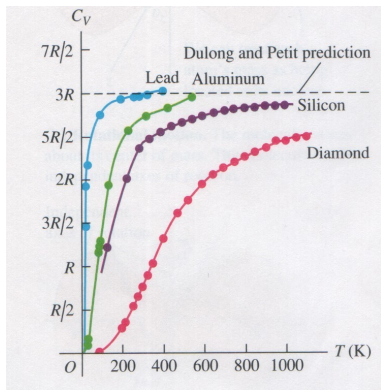
Thus, the *molar* heat capacity

$$c_V = 3R \quad \text{independently of the material}$$

This is known as a *Dulong and Petit* law.

HEAT CAPACITIES OF CRYSTALLINE SOLIDS II

Dulong and Petit law holds well for high enough temperatures.



To explain the low-temperature behaviour, one again needs quantum mechanics.
(and in the low- T regime different materials behave differently)