Boltzmann's Constant and Gas Constant

Basics

- We have repeatedly stressed the fact that whenever you encounter Boltzmann's constant **k** we deal with the particle unit "atom" or "molecule", while whenever we encounter the gas constant **R**, we deal with the the unit "mol". Here we will quickly survey the connection.
  - First we have the general law for ideal gases with volume ***V***, pressure ***p*** and temperature ***T***

$$p \cdot V = \text{const} \cdot T$$

  - This was first an empirical law that later became fully understood by statistical thermodynamics.
- The next step is to realize that if you increase the volume while keeping everything else constant, the "const" in the law must increase in the same proportion. This leads to the much more universal formulation that is generally used:

$$p \cdot V = n \cdot R \cdot T$$

  - With n = quantity of the gas, and **R** = gas constant with a value depending on how you measure **n**.
- This would still leave room for **R** being different for different kind of gases. **Avogadro** enters, proposing that identical volumina of gases under identical pressure and temperature contain identical numbers of particles.
- This permits to define **R** for all (ideal) gases and to measure it. We find

$$R = \frac{p \cdot V}{n_{mol} \cdot T} = 8.32441\ J \cdot K^{-1} \cdot mol^{-1}$$

  - *if* me measure the quantity n of the gas in *mols*. º
  - One **mol** of a substance, *per definition*, contains just as many particles, objects, or building blocks of that substance (i.e. atoms, molecules, electrons, vacancies, ...), as there are carbon atoms in **1 g** of ^{12}C which gives

$$1\ mol = 6.022 \cdot 10^{23}$$

  - **Avogadros constant** then automatically is

$$N_A = 6.022 \cdot 10^{23}\ mol^{-1}$$

  - i.e. we have $6.022 \cdot 10^{23}$ particles *per mol* of a substance.
- If we set $n = 1$ we have for the mol-volume V_m, i.e. for the volume that **1** mol of a gas occupies

$$V_m = \frac{n \cdot R \cdot T}{p} = 22.414\ \frac{l}{mol}$$

  - This is valid for for "old" standard conditions (p **= 1013 mbar = 101 325 Pa**, and $T = 0^oC$).
  - For the "new" standard conditions (p **= 100 000 Pa**, T **= 298.15 K**) we have V_m **= 24.789 l/mol**
  - *Why the international standards and units of measurements must change all the time is beyond me, but that's the way it is. I have suffered through **4** changes in the units for pressure by now, not to mention the big pain caused by the fact that the Americans normally don't care and still stick to **psi**.*
- If we now measure substance quantities not per mol, but per particle, we must divide **R** by Avogadros constant N_A and obtain

$$p \cdot V = n_{part} \cdot \frac{R}{N_A} \cdot T = n_{part} \cdot kT$$

- and n_{part} is now the *number of particles* in ***V***.
- For R/N_A =: **k = Boltzmann's constant** we obtain

$$k = \frac{8.32441}{6.022 \cdot 10^{23}} \; J \cdot K^{-1} = 8.616 \cdot 10^{-5} eV \cdot K^{-1}$$

Fine, we can see that as a *definition* of Boltzmann's constant **k**. But now we have two questions:

- **1.** Why is the **k** from the gas law the same number as in the famous entropy equation $S = k \cdot \ln P$?
- *Not obvious* - and not exactly easy to prove. Essentially, you have to unleash the full power of statistical thermodynamics to show that both **k's** are identical. So either grab your thermodynamic textbook, or believe your professor at this point.
- **2**. Is there a way to calculate the numerical value of **k** from some more fundamental constants? Well, as far as I know, it *cannot be done*. So **k** is a basic *constant of nature*, in the same league as other fundamental constants of nature, like the speed of light, the gravitational constant, or the elementary charge.

Finally something to make things really complicated:

- Changing from *mols* to *particle numbers* or *densities*, changes the precise formulation of the mass action law. Consult the link for details.