Kinetic Theory and Thermodynamics

Notes by Paul Walsh
pwalsht@maths.tcd.ie

Reciprocal Relation

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z^{-1}$$

Cycical Rule

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Chain Rule

$$\left(\frac{\partial x}{\partial z}\right)_\phi = \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial z}\right)_\phi$$

Most of the time, x, y, and z will be replaced by P, V, and T respectively.

Van Der Waal's Equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The constants a and b are empirical constants, different for different gases. Roughly speaking, b represents the volume of a mole of molecules; the total volume of the molecules is then nb, and the net volume available for the molecules to move around in is $V - nb$. The constant a depends on the attractive intermolecular forces, which reduce the pressure of the gas for given values of n, V, and T by *pulling* the molecules together as they *push* on the walls of the container. The decrease in pressure is proportional to the number of molecules per unit volume in a layer near the wall (which are exerting the pressure on the wall) and is also proportional to the number per unit volume in the next layer beyond the wall (which are doing the attracting). Hence the decrease in pressure due to intermolecular forces is proportional to n^2/V^2.

Average Kinetic Energy ($K.E._{tr}$) of n moles of an ideal gas

$$K_{tr} = \frac{3}{2}nRT$$

Average Kinetic Energy of a gas molecule

$$\frac{1}{2}m(v^2)_{avg} = \frac{3}{2}kT$$

Root-mean-square speed

$$V_{r.m.s.} = \sqrt{(v^2)_{avg}} = \sqrt{\frac{3kT}{m}}$$

Mean-free time

$$t_{mean} = \frac{V}{4\pi\sqrt{2}r^2vN}$$

where when we consider N spherical molecules with radius r in a volume V.

Mean-free path of a gas molecule

$$\lambda = vt_{mean} = \frac{V}{4\pi\sqrt{2}r^2N}$$

Molar heat capacity at constant volume for an ideal gas of point particles

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

Principle of Equipartition of Energy

This principle states that each velocity component (either linear or angular) has on average, an associated kinetic energy per molecule of $1/2kT$, or one half the product of the Boltzmann constant and the absolute temperature. The number of velocity components needed to describe the motion of a molecule completely is called the number of **degrees of freedom**. For a monatomic gas, there are three degrees of freedom; this gives a total kinetic energy of $3(1/2kT)$. For a *diatomic* molecule there are two possible axes of rotation, perpendicular to each other and to the molecule's axis. If five degrees of freedom are assigned to a diatomic molecule, the average total kinetic energy per molecule is $5/2kT$ instead of $3/2kT$.

$$C_V = \frac{5}{2}R$$

for a diatomic gas, including rotation.

If you detect any errors in these notes pls cont act me at pwalsht@maths.tcd.ie and I will try to amend them.

Notes after this point currently being drafted.