CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11^{th} Edition, Oxford University Press.

Reference books

. Physical Chemistry, Robert J. Silbey, Robert A. Alberty, Moungi G. Bawendi

. Physical Chemistry, Ira N. Levine

B. The kinetic model

The Maxwell-Boltzmann distribution of speeds: an expression for the distribution of the kinetic energy;

$$f(v) = Ke^{-\epsilon/kT}$$

where K is a constant of proportionality. The kinetic energy is

$$\epsilon = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

$$f(v) = Ke^{-(mv_x^2+mv_y^2+mv_z^2)/2kT} = Ke^{-mv_x^2/2kT}e^{-mv_y^2/2kT}e^{-mv_z^2/2kT}$$

$$f(v_x) = K_x e^{-mv_x^2/2kT}$$ *(for x coordinate)*

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B. The kinetic model

Determine the constants K_{x}, K_{y} and K_{z}

To determine the constant K_x, note that a molecule must have a velocity component somewhere in the range $-\infty < v_x < \infty$, so integration over the full range of possible values of v_x must be a total probability of 1:

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1$$

For $f(v_x)$

$K_x = (m/2\pi kT)^{1/2}$ and

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

The expressions for $f(v_y)$ and $f(v_z)$ are analogous.

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B. The kinetic model

Write a preliminary expression for $f(v_x)\,f(v_y)\,f(v_z)\,dv_x\,dv_y\,dv_z$.

The probability that a molecule has a velocity in the range v_x to v_x+dv_x, v_y to v_y+dv_y, v_z to v_z+dv_z is

$$f(v_x)f(v_y)f(v_z)dv_x\,dv_y\,dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} \overbrace{e^{-mv_x^2/2kT}e^{-mv_y^2/2kT}e^{-mv_z^2/2kT}}^{e^{-m\left(v_x^2+v_y^2+v_z^2\right)/2kT}} * dv_x dv_y dv_z$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} dv_x dv_y dv_z$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$

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B. The kinetic model

Calculate the probability that a molecule has a speed in the range **v to v+dv**

. think three velocity components

. three coordinate velocity space

. think the volume of a spherical shell of radius r and thickness dr. That volume is $4\pi r^2 dr$. For velocity space (analogous to that volume) $4\pi v^2 dr$.

If probability is written for f(v)dv

$$f(v)dv = 4\pi v^2 dv \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$$

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B. The kinetic model

and f(v) itself, after minor rearrangements , is

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

Because $R=N_A k$, $m/k = mN_A/R=M/R$

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

Maxwell-Boltzmann distribution (KMT)

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