

Chemistry 4000/5000/7001 Spring 2009 Test 2 Solutions

1. The internal energy of an ideal monatomic gas is all kinetic. The kinetic energy is

$$K = \frac{1}{2}mv^2,$$

so the molar internal energy would be the average K times Avogadro's number, i.e.

$$U_m = \frac{1}{2}N_A m \langle v^2 \rangle = \frac{1}{2}M \langle v^2 \rangle.$$

The mean squared speed is given by the kinetic theory as

$$\langle v^2 \rangle = 3RT/M,$$

so the molar internal energy is

$$U_m = \frac{1}{2}M \left(\frac{3RT}{M} \right) = \frac{3}{2}RT.$$

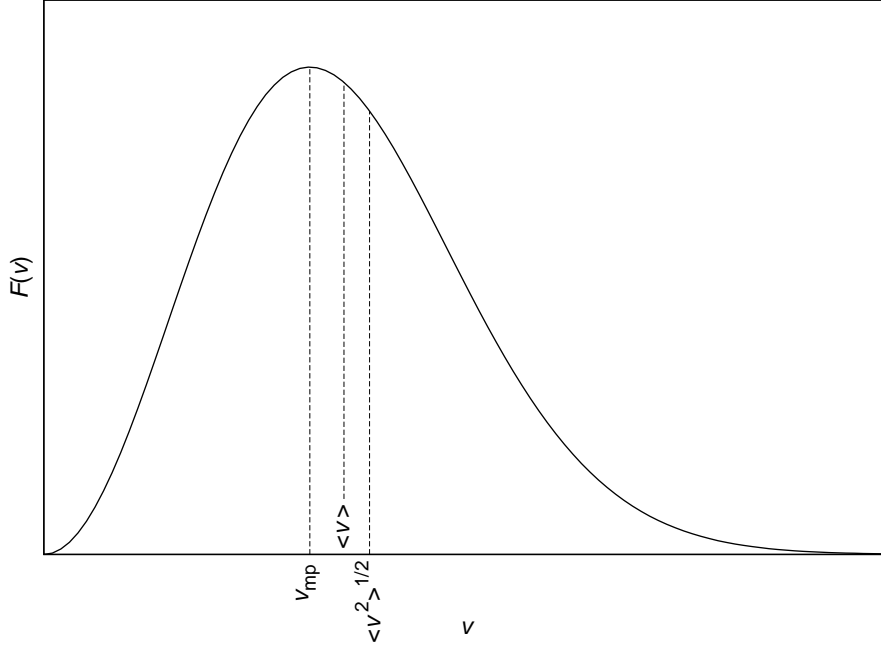
2. (a) An ideal rubber is one for which $\left. \frac{\partial U}{\partial L} \right|_{T,V} = 0$.

- (b) The force required to hold an ideal rubber at an extension L is given by

$$f = -T \left. \frac{\partial S}{\partial L} \right|_{T,V}.$$

In a rubber, extending the material causes conformational changes in the bonds tending to align them (on average) with the extension. S thus decreases with L , causing a reaction force which opposes further stretching. The basis of this effect is that there are many more microstates in directions of internal motion leading toward the relaxed state than in directions leading toward the extended state. Random thermal motions are thus much more likely to “pull back” toward the relaxed state than otherwise.

3.



4. The probability is calculated by

$$P(v > 800 \text{ m/s}) = \int_{800 \text{ m/s}}^{\infty} F(v) dv,$$

where

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

In this case, $M = 28.0134 \times 10^{-3} \text{ kg/mol}$. The other constants (R and T) are as given in the test paper. We get

$$P(v > 800 \text{ m/s}) = 0.5406.$$

5. (a) $\langle v \rangle = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(77 \text{ K})}{\pi(2.015 \text{ 650 064} \times 10^{-3} \text{ kg/mol})}} = 899 \text{ m/s}$

(b) $\langle v \rangle = \sqrt{\frac{8(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(77 \text{ K})}{\pi(3.021 \text{ 926 810} \times 10^{-3} \text{ kg/mol})}} = 734 \text{ m/s}$

(c) The rate of effusion is

$$\frac{dN_c}{dt} = \frac{1}{4} \tilde{N} A \langle v \rangle.$$

The particle density is

$$\tilde{N} = \frac{N}{V} = \frac{P}{kT}.$$

The area of the aperture is $A = \pi r^2$. Putting these relationships into the effusion rate and rearranging, we get

$$\begin{aligned}
 P &= \frac{4kT(dN_c/dt)}{\pi r^2 \langle v \rangle} \\
 &= \frac{4(1.380\,650\,4 \times 10^{-23} \text{ J/K})(77 \text{ K})(10^{16} \text{ s}^{-1})}{\pi(0.2 \times 10^{-3} \text{ m})^2(899 \text{ m/s})} = 0.38 \text{ Pa.}
 \end{aligned}$$

6.

- **The solvent can be described as occupying a lattice.** This is probably not a serious approximation. While liquids do have some disorder, intermolecular forces maintain some local order.
- **The polymer can be broken down into segments which occupy an array of contiguous solvent lattice sites.** This is a much more doubtful approximation. The geometry of the polymer may be such that its configurations cannot be described by “threading” it through a lattice of the same geometry as the solvent.
- **Only nearest-neighbor interactions are important.** This may or may not be a good approximation. If we have a solvent with a large dipole moment, or strongly polar groups on the polymer, then we would expect that interactions other than nearest-neighbor interactions might be important. At the other extreme, the case of a nonpolar polymer in a nonpolar solvent, it should be a reasonable approximation since van der Waals forces have a very short range.
- **Only the conformational entropy of the polymer matters.** Of course, local changes in polymer structure on entering solution can also contribute to the change in entropy, among other factors. This is probably not a very good approximation for polymers that have a lot of conformational flexibility beyond the monomer-to-monomer linkages.
- **Self-avoidance is not properly taken into account in the entropy calculation.** In other words, we don’t take into account the fact that a site adjacent to one monomer is likely to be occupied by another monomer from the same polymer due to bends in the polymer conformation. This is a small correction however.