CHM328S: Modern Physical Chemistry

Problem Set 2: Applications of Kinetic Theory

Notes:

- Please start each problem on a new page.
- This problem set is due on Thursday, February 26, 2009.

1. Suppose that a gas inside a container of volume V at temperature T obeys the ideal gas law. Show that if a small hole of area A_0 is made in the container and the gas is not replenished, then the pressure of the gas drops from the initial pressure P_0 according to the law

$$P = P_0 e^{-t/\tau}.$$

   Obtain an expression for τ in terms of the mass of the gas, the temperature T, the volume V and area of the hole A_0.

2. As an application of the previous system, consider a container containing Cesium (m.p 29 C, b.p. 686 C) that is heated to 500 C. When a hole of diameter 0.5 mm was opened in the container for 100 seconds, a mass loss of 358 mg was measured. Note that the pressure of the vapor inside the container is constant since the hot liquid metal replaces the vapor as it escapes through the hole.

   (a) What is the relation between the collision frequency of Cesium atoms and the wall Z_w and the mass loss Δm?

   (b) Calculate the vapor pressure of liquid Cesium at 500 C.

   (c) How long would it take for 1.0 g of Cs atoms to effuse out of the oven under these conditions?

3. Calculate the collision frequency and mean free path of argon atoms (effective diameter of $d = 2.86$ Angstroms) at standard temperature and pressure. How many collisions take place per atom per second? How many collisions take place per second in 1 cm^3?

4. An important “transport” property is the self-diffusion coefficient D, defined by noting that the average distance squared a particle moves in an interacting system grows linearly with time at long times according to

$$\langle |\boldsymbol{r}(t) - \boldsymbol{r}(0)|^2 \rangle = 6Dt.$$

   (a) Noting that ν is the average collision frequency per particle and that νdt is the probability that a given particle collided with another in a time interval dt, show that for small time intervals dt, the probability $P(t)$ that a given particle hasn't collided at time t measured from an initial time $t = 0$ is given by

$$P(t) = P(t - dt)(1 - \nu dt)$$

   provided the probability of a particle undergoing a collision in a given time interval is independent of time.

   (b) Obtain a differential equation for $P(t)$ in the limit that dt goes to zero.

   (c) Show that $P(t)$ and the complement of $P(t)$, $P_c(t) = 1 - P(t)$, are given by:

$$P(t) \;=\; e^{-\nu t} \qquad P_c(t) = 1 - e^{-\nu t}.$$

   (d) What is the physical interpretation of $P_c(t)$?

   (e) Defining the probability density for collisions $\rho(t)$ via

$$P_c(t) \;=\; \int_0^t \rho(\tau) d\tau,$$

   show that $\rho(t) = \nu \exp -\nu t$. What is the physical significance of $\rho(\tau)d\tau$?.

   (f) What is the average “free flight time”, or time duration between collision, t_f?

   (g) By noting that $\boldsymbol{r}(t) = \boldsymbol{r}(0) + \boldsymbol{v}t$ for hard spheres between collision events, what is the average squared-distance $\overline{|\boldsymbol{r}(t) - \boldsymbol{r}(0)|^2}$ (over $\rho(t)$ and the distribution of velocities) that a particle travels before collisions?

   (h) If we define $D = \overline{|\boldsymbol{r}(t) - \boldsymbol{r}(0)|^2}/(6t_f)$, what is the self-diffusion coefficient D?

   (i) In this treatment, we supposed that the collision frequency $\nu(\boldsymbol{v})$ of a particle moving with velocity $\boldsymbol{v}$ was the average collision frequency ν. Is this true? Why, or why not?