Additional Comments to Gaseous Diffusion Experiment

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January, 2004

The “derivation” included in the instruction manual of the gaseous diffusion experiment is extremely unsatisfactory. This hand-out clears up some of the ambiguities.

Consider the capillary with acetone. We denote point “1” as the top, where the air is blowing past. At point 1, the concentration of acetone is assumed to be zero. We denote point “2” as the air/liquid acetone interface. At point 2, the concentration of acetone is assumed to be in equilibrium with the liquid acetone. Let us denote air as B and acetone as A. These choices of 1, 2, A, and B correspond to the same choices made in the lab manual, although these definitions are never clearly stated in the manual.

We will assume that the entire capillary is at the temperature of the external water bath, T. We will also assume that the pressure is constant in the capillary at ambient pressure, p.

We will use the ideal gas law to calculate molar volumes.

$$pV = NRT \tag{1}$$

At the top of the capillary, at point 1, the total concentration is given as

$$c_{T,1} = \frac{N}{V} = \frac{p}{RT} \tag{2}$$

The mole fraction of air and acetone are respectively,

$$x_{B,1} = 1.0 \tag{3}$$

$$x_{A,1} = 0.0 \tag{4}$$

Therefore, the concentrations of A and B at point 1 are

$$c_{B,1} = x_{B,1} \cdot c_{T,1} = c_{T,1} \tag{5}$$

$$c_{A,1} = x_{A,1} \cdot c_{T,1} = 0 \tag{6}$$

At the gas/liquid interface, at point 2, the total concentration is given as

$$c_{T,2} = \frac{N}{V} = \frac{p}{RT} = c_{T,1} \tag{7}$$

In order to determine the mole fraction of air and acetone at the interface, we will take advantage of our dear and abiding friendship with Raoult’s law, which states in an approximate manner

$$z_A p_A^{vap}(T) = x_{A,2} p \tag{8}$$

where z_A is the mole fraction of component A in the liquid phase and $p_A^{vap}(T)$ is the vapor pressure of pure component A at the temperature of the bath. We will assume for the time being that we know the vapor pressure. This will be discussed later on this handout. In this experiment we will assume that the liquid is pure acetone, in which case $z_A = 1$. As a result, the mole fraction of acetone at the gas/liquid interface is

$$x_{A,2} = \frac{p_A^{vap}(T)}{p} \tag{9}$$

The mole fraction of air is

$$x_{B,2} = 1 - x_{A,2} = 1 - \frac{p_A^{vap}(T)}{p} = \frac{p - p_A^{vap}(T)}{p} \tag{10}$$

Therefore, the concentrations of A and B at point 2 are

$$c_{B,2} = x_{B,2} \cdot c_{T,2} = \frac{p - p_A^{vap}(T)}{p} c_{T,2} \tag{11}$$

$$c_{A,2} = x_{A,2} \cdot c_{T,2} = \frac{p_A^{vap}(T)}{p} c_{T,2}$$

We do not derive in this version of the experimental supplement the fact that the proper value of the concentration of air to me used in this experiment is the log-mean concentration.

$$c_{B,lm} = \frac{c_{B,1} - c_{B,2}}{\ln\left(\frac{c_{B,1}}{c_{B,2}}\right)} \tag{12}$$

A derivation of equation (12) is available from BSL2.

Bird, R.B., Steward, W.E., Lightfoot, E.N., Transport Phenomena, 2nd Ed., John Wiley & Sons, Inc. New York, 2002, p. 545-547.

BSL2 (p. 548) also derives the expression for the molar flux due to diffusion of A at the interface, point 2.

$$N_{A,2} = \frac{c_{T,2}D_{AB}}{c_{B,lm}}\frac{c_{A,2} - c_{A,1}}{L} \tag{13}$$

The molar flux due to evaporation of A at the interface, point 2, is given by

$$N_{A,2} = \frac{\rho_A}{MW_A}\frac{dL}{dt} \tag{14}$$

where ρ_A is the mass density of pure liquid A at temperature T.
We equate these two fluxes, since the system is at steady state. They can be integrated because only L changes as a function of time. All the densities, concentrations, molecular weights and diffusivities are constant and can be pulled outside the integral.

$$\frac{c_{T,2}D_{AB}MW_A}{\rho_A c_{B,lm}}\left(c_{A,2} - c_{A,1}\right)\int_{t_o}^{t} dt = \int_{L_o}^{L} LdL \tag{15}$$

$$\frac{2c_{T,2}D_{AB}MW_A}{\rho_A c_{B,lm}}\left(c_{A,2} - c_{A,1}\right)\left(t - t_o\right) = L^2 - {L_o}^2 \tag{16}$$

We can measure only $L - L_o$ accurately. We rewrite the right-hand-side as

$$L^2 - {L_o}^2 = \left(L - L_o\right)\left(L + L_o\right) = \left(L - L_o\right)\left(L - L_o + 2L_o\right) = \left(L - L_o\right)^2 + 2\left(L - L_o\right)L_o \tag{17}$$

$$\frac{2c_{T,2}D_{AB}MW_A}{\rho_A c_{B,lm}}\left(c_{A,2} - c_{A,1}\right)\left(t - t_o\right) = \left(L - L_o\right)^2 + 2\left(L - L_o\right)L_o \tag{18}$$

We can manipulate this further to yield

$$\frac{\left(t - t_o\right)}{\left(L - L_o\right)} = S\left(L - L_o\right) + 2SL_o \tag{19}$$

where

$$S = \frac{\rho_A c_{B,lm}}{2c_{T,2}D_{AB}MW_A\left(c_{A,2} - c_{A,1}\right)} \tag{20}$$

Note that everything inside S is a constant.

So if you plot $\frac{(t-t_o)}{(L-L_o)}$ as a function of $(L-L_o)$. The plot should be linear. The slope will be equal to S. Once we know S, we can solve for the diffusivity.

$$D_{AB} = \frac{\rho_A c_{B,lm}}{2 S c_{T,2} MW_A \left(c_{A,2} - c_{A,1}\right)} \qquad (21)$$

If you want to see the derivation for equations (12), (13), and (14), see the instructor for a copy of the pertinent pages from BSL2.

Vapor Pressure

One can use the Antoine Equation to calculate the vapor pressure of acetone.

The Antoine Equation is

$$\log_{10}(p) = A - \frac{B}{T + C} \tag{22}$$

where
p = vapor pressure (bar)
T = temperature (K)

acetone parameters:

A = 4.42448
B = 1312.253
C = -32.445

accurate in a temperature range from 259.16 - 507.60 K
Coefficents calculated by NIST (http://webbook.nist.gov/chemistry/) from data available in

Ambrose, D.; Sprake, C.H.S.; Townsend, R., *Thermodynamic Properties of Organic Oxygen Compounds. XXXIII. The Vapour Pressure of Acetone*, **J. Chem. Thermodyn.**, 1974, 6, 693-700.