Rizzo, Jonathan

From:	Szalda, Bryan <Bryan.Szalda@ghd.com>
Sent:	Thursday, May 4, 2017 4:31 PM
To:	Rizzo, Jonathan
Subject:	FW: Document
Attachments:	20170427112330490.pdf

Jonathan –

Just a note that I sent this over to Mike. I will call him tomorrow to walk him through it.

From: Szalda, Bryan
Sent: Thursday, May 04, 2017 4:30 PM
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Subject: Document

Mike ---

See attached. We can discuss tomorrow after you've had a chance to go through it.

Bryan

Table 7-2
Models used for estimating molecular diffusion coefficients in liquids

Application	**Model**	**Comments**
Large spherical molecules or particles	Stokes–Einstein equation: $D_l = \frac{kT}{3\pi\mu_l d_m}$	Diffusion coefficients are slightly larger than measured values for large spherical molecules (MW > 1000 Da) or particles in liquids. Diffusivity for small molecules with MW on order of 100 Da is underestimated.
For nonelectrolytes and small molecules	Hayduk–Laudie correlation: $D_l = \frac{13.26 \times 10^{-9}}{(\mu_l)^{1.14}(V_b)^{0.589}}$	Hayduk and Laudie (1974); convert units for μ_l to cP and use Table 7-3 for V_b (cm^3/mol), D_l is expressed in units of m^2/s.
For electrolytes in absence of electric field	Nernst–Haskell equation: $D_{AB} = \frac{RT}{F^2}\left[\frac{1/n^+ + 1/n^-}{1/\lambda_+^0 + 1/\lambda_-^0}\right]$	Poling et al. (2001); use Table 7-4 for λ values.

where D_l = liquid-phase diffusion coefficient at 20°C, m^2/s
k = Boltzmann constant, 1.381×10^{-23} J/K (N-m/K)
T = absolute temperature, K (273 + °C)
μ_l = liquid viscosity at 20°C, 1.00×10^{-3} N·s/m^2
d_m = molecular diameter, m

Equation 7-30 is valid only for spherical molecules.

The validity of the Stokes–Einstein equation can be evaluated by comparing it against measured values of diffusion coefficients for proteins. Polson (1950) correlated experimental data for globular proteins and obtained the empirical expression:

$$D_l = 2.74 \times 10^{-9}\,(\mathrm{MW})^{-1/3} \tag{7-31}$$

where D_l = liquid-phase diffusion coefficient, m^2/s
MW = molecular weight, Da or g/mol

The molecular density of a globular protein is about 1.35 g/cm^3, so a protein molecule with a MW of 50,000 Da has a diameter of about 4.9 nm (i.e., MW = number of molecules per mole × density of a molecule × volume of a molecule). Substituting this value into Eq. 7-30 results in a diffusion coefficient of 8.8×10^{-11} m^2/s, compared to a value of 7.4×10^{-11} m^2/s calculated by Eq. 7-31. Thus, the value calculated with the Stokes–Einstein equation is about 15 percent higher than the calculated value. The similarity of the two values is noteworthy considering that the Stokes–Einstein equation is derived from first principles and Eq. 7-31 is an empirical expression.

Liquid-Phase Diffusion Coefficients for Small Neutral Molecules

The diffusivities of small uncharged molecules (such as synthetic organic chemicals) in water can be calculated using the Hayduk–Laudie correlation (Hayduk and Laudie, 1974), which is a revised version of a correlation developed by Othmer and Thakar (1953). The Hayduk–Laudie correlation is an empirical equation given by

$$D_l = \frac{13.26 \times 10^{-9}}{(\mu_l)^{1.14}(V_b)^{0.589}} \tag{7-32}$$

where D_l = liquid-phase diffusion coefficient of solute, m^2/s
μ_l = viscosity of water, cP (1 cP = 10^{-3} kg/m·s)
V_b = molar volume of solute at normal boiling point, cm^3/mol

Because the Hayduk–Laudie correlation was developed as a regression of experimental data and is not dimensionally consistent, it is important to use the units given for the equation. The molar volume at the normal boiling point, V_b, can be estimated using the LeBas method (LeBas, 1915). The atomic volumes for different elements, mixtures, and functional groups for use in calculation of molar volume at the normal boiling point via the LeBas method are presented in Table 7-3. Contributions of the various functional groups are added together along with deductions for certain ring structures. Calculation of the diffusion coefficient of a small neutral molecule using the Hayduk–Laudie correlation is illustrated in Example 7-1.

Liquid-Phase Diffusion Coefficients for Electrolytes

Electroneutrality requires that positive and negative ions migrate together, so diffusion coefficients are calculated for electrolytes (solutions of charged ions) instead of being calculated for each ion individually. As an example, the values of diffusion coefficients in Table 7-1 demonstrate that sodium and magnesium each diffuse faster when the counterion is chloride than when it is sulfate. In the absence of an electric field, diffusion of ions will generate an electric current in a solution. Conversely, the current through a unit area that results from applying an electric field for a given electrolyte concentration is known as the equivalent conductance. Thus, liquid-phase diffusion coefficients of electrolytes in the absence of an electric field are related to the equivalent conductance and can be calculated using the Nernst–Haskell equation:

$$D_l^\circ = \frac{RT}{F^2}\left(\frac{1/n^+ + 1/n^-}{1/\lambda_+^\circ + 1/\lambda_-^\circ}\right) \tag{7-33}$$

where D_l° = liquid-phase diffusion coefficient at infinite dilution, cm^2/s
R = universal gas constant, 8.314 J/mol·K
T = absolute temperature, K (273 + °C)

Table 7-3

Atomic volumes for use in computing molar volumes at normal boiling point with LeBas method

Element, Mixture, or Functional group	Atomic Volume, cm^3/mol	Circumstance	Element, Mixture, or Functional group	Atomic Volume, cm^3/mol	Circumstance
Air	29.9		Oxygen	7.4	Doubly bond, as carbonyl oxygen
Antimony	34.2			7.4	In aldehydes or ketones
Arsenic	30.5			9.1	In methyl esters
Bismuth	48.0			9.9	In methyl ethers
Bromine	27.0			11.0	In higher ethers and esters
Carbon	14.8			12.0	In acids
Chlorine	21.6	Terminal as in R—Cl		8.3	In union with S, P, or N
		Medial as in R—CHCl—R	Phosphorus	27.0	
Chromium	27.4		Silicon	32.0	
Fluorine	8.7		Sulfur	25.6	
Germanium	34.5		Tin	42.3	
Hydrogen	3.7	In organic compound	Titanium	35.7	
	7.15	In hydrogen molecule	Vanadium	32.0	
Iodine	37.0		Water	18.8	
Lead	46.5–50.1		Zinc	20.4	
Mercury	19.0		Ring deductions	6.0	Three-membered ring
Nitrogen	15.6			8.5	Four-membered ring
	10.5	In primary amines		11.5	Five-membered ring
	12.0	In secondary amines		15	Six-membered ring
				30	Naphthalene ring
				47.5	Anthracene ring

Source: Adapted from LeBas (1915).

z^+ = cation valence
z^- = anion valence
F = Faraday's constant, 96,500 C/eq
λ_+° = limiting positive ionic conductance, cm^2-s/eq
λ_-° = limiting negative ionic conductance, cm^2-s/eq

Values for limiting positive ionic conductance at 25°C are tabulated in Table 7-4. Values at other temperatures are available in reference books such as Robinson and Stokes (1959). The limiting ionic conductance is related to electric current and electric field strength in an infinitely dilute

Example 7-1 Estimating the diffusion coefficient for small neutral molecules in water

Estimate the diffusion coefficients of the following contaminants found in a groundwater: (1) vinyl chloride at 25°C and (2) benzene at 20°C. Use Table 7-3 to find the contributions of the various functional groups to the molar volume. Density and viscosity of water are available in App. C [convert the given units of viscosity to g/cm·s, i.e., centipoise (cP)]. Compare the values to the measured values reported in Table 7-1.

Solution

1. Calculate the liquid-phase diffusion coefficient for vinyl chloride.
   a. Estimate the molar volume at the boiling point using the information in Table 7-3. The chemical formula for vinyl chloride is C_2H_3Cl. The contribution of each atom to the molar volume is

$$2\text{C} = 2\,(14.8) = 29.6\ \text{cm}^3/\text{mol}$$
$$3\text{H} = 3\,(3.7) = 11.1\ \text{cm}^3/\text{mol}$$
$$\text{Cl} = (21.6) = 21.6\ \text{cm}^3/\text{mol}$$

   The molar volume is determined by adding the contributions of each atom:

$$V_b = 29.6 + 11.1 + 21.6 = 62.3\ \text{cm}^3/\text{mol}$$

   b. Calculate the diffusion coefficient using Eq. 7-32. The viscosity of water at 25°C is 0.89×10^{-3} kg/m·s = 0.89 cP.

$$D_l = \frac{13.26 \times 10^{-9}}{(0.89\ \text{cP})^{1.14}\,(62.3\ \text{cm}^3/\text{mol})^{0.589}} = 1.33 \times 10^{-9}\ \text{m}^2/\text{s}$$

   c. Compare the calculated value to the measured value in Table 7-1.

$$\frac{1.34 \times 10^{-9} - 1.33 \times 10^{-9}}{1.34 \times 10^{-9}} \times 100 = 1\%\ \text{error}$$

2. Calculate the liquid phase diffusion coefficient for benzene.
   a. Benzene is an aromatic compound (6 carbon ring) with the chemical formula C_6H_6. The contribution of each atom to the molar volume is

$$6\text{C} = 6\,(14.8) = 88.8\ \text{cm}^3/\text{mol} \quad 6\text{H} = 6\,(3.7) = 22.2\ \text{cm}^3/\text{mol}$$

$$\text{Six-member ring} = -15\ \text{cm}^3/\text{mol}$$

   The molar volume is determined by adding the contributions of each atom:

$$V_b = 88.8 + 22.2 - 15 = 96\ \text{cm}^3/\text{mol}$$

b. Calculate the diffusion coefficient using Eq. 7-32. The viscosity of water at 20°C is 1.00×10^{-3} kg/m · s = 1.00 cP.

$$D_l = \frac{13.26 \times 10^{-9}}{(1.00\ \text{cP})^{1.14}\,(96\ \text{cm}^3/\text{mol})^{0.589}} = 0.90 \times 10^{-9}\ \text{m}^2/\text{s}$$

c. Compare the calculated value to the measured value in Table 7-1.

$$\frac{1.02 \times 10^{-9} - 0.90 \times 10^{-9}}{1.02 \times 10^{-9}} \times 100 = 11\%\ \text{error}$$

Comment

The value estimated with the Hayduk–Laudie correlation is within 1 percent of the measured value for vinyl chloride and within 11 percent of the measured value for benzene. These results are typical; the Hayduk–Laudie correlation is often within 10 percent of measured values for many compounds (it should be noted that measured values by different researchers with different methods also vary). As a result of this level of accuracy, it is common to estimate liquid-phase diffusion coefficients with the Hayduk–Laudie correlation rather than obtaining measured values for the species of interest.

Table 7-4
Limiting ionic conductances in water at 25°C [$\text{cm}^2 \cdot \text{S/eq}$ or $(\text{cm}^2\text{-C}^2)/(\text{J-s-eq})$]

Cation	Formula	λ_+°	Anion	Formula	λ_-°
Hydrogen	H^+	349.8	Hydroxide	OH^-	199.1
Lithium	Li^+	38.6	Fluoride	F^-	55.4
Sodium	Na^+	50.1	Chloride	Cl^-	76.4
Potassium	K^+	73.5	Bromide	Br^-	78.1
Rubidium	Rb^+	77.8	Iodide	I^-	76.8
Cesium	Cs^+	77.2	Bicarbonate	HCO_3^-	44.5
Ammonium	NH_4^+	73.5	Nitrate	NO_3^-	71.5
Silver	Ag^+	61.9	Perchlorate	ClO_4^-	67.3
Magnesium	Mg^{2+}	53.0	Bromate	BrO_3^-	55.7
Calcium	Ca^{2+}	59.5	Formate	$HCOO^-$	54.5
Strontium	Sr^{2+}	59.4	Acetate	CH_3COO^-	40.9
Barium	Ba^{2+}	63.6	Chloroacetate	$ClCH_2COO^-$	42.2
Copper	Cu^{2+}	53.6	Propionate	$CH_3CH_2COO^-$	35.8
Zinc	Zn^{2+}	52.8	Benzoate	$C_6H_5COO^-$	32.3
Lead	Pb^{2+}	69.5	Carbonate	CO_3^{2-}	69.3
Lanthanum	La^{3+}	69.7	Sulfate	SO_4^{2-}	80.0

Ref: Robinson and Stokes (1959).