Appendix B

HENRY'S LAW CONSTANT - EQUATIONS

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The calculation of Henry's law constant for a component in water may be achieved using data for solubility, vapor pressure, and activity coefficient at infinite dilution. The derivation of the appropriate equations is briefly given in the following discussion.

LIQUIDS (PARTIAL SOLUBILITY)

For organic chemicals that are liquids at ambient conditions and have partial solubility in water, there are three phases when the organic chemical is in contact with water. These are vapor, organic, and water phases. Such a three-phase system consisting of vapor, liquid I and liquid II is shown in Fig. B-1a. At equilibrium, the fugacity of the component in each liquid phase is

$$f_i^{liq\ I} = f_i^{liq\ II} \qquad \text{(B-1)}$$

For the organic phase (liquid I), the fugacity of the component is γ_i * mol fraction$_i$ * vapor pressure$_i$ (where γ_i is the activity coefficient). Since the organic phase has only very small concentration of water (ppm level or less), the mol fraction of the organic chemical is approximately equal to 1 (mol fraction$_i \approx 1$). This is also true for the activity coefficient of the organic chemical ($\gamma_i \approx 1$). Thus

$$f_i^{liq\ I} = P_i^{SAT} \qquad \text{(B-2)}$$

For the water phase (liquid II), the fugacity of the component is given by Henry's law which is applicable at very small concentration. The equation is

$$f_i^{liq\ II} = H_i\, x_i^{liq\ II} \qquad (x_i << 1) \qquad \text{(B-3)}$$

Substitution of Equations (B-2) and (B-3) into Equation (B-1) yields

$$P_i^{SAT} = H_i\, x_i^{liq\ II} \qquad \text{(B-4)}$$

Solving for Henry's law constant yields the following equation which is applicable to organic chemicals which are liquids at ambient conditions (25 C, 1 atm) and have only small partial solubility in water:

$$H_i = (\,1 / x_i^{liq\ II}\,)\, P_i^{SAT} \qquad \text{(B-5)}$$

where H_i = Henry's law constant, atm/mol fraction
$x_i^{liq\ II}$ = solubility of organic chemical in water, mol fraction
P_i^{SAT} = vapor pressure of organic chemical, atm

LIQUIDS (TOTAL SOLUBILITY)

For organic chemicals that are liquids at ambient conditions and have total solubility in water, there are two phases when the organic chemical is in contact with water. These are vapor and liquid phases. Fig. B-1b shows such a two-phase system.

For the liquid phase, the fugacity of the organic chemical is γ_i * mol fraction$_i$ * vapor pressure$_i$ (where γ_i is the activity coefficient). Since the liquid phase has only very small concentration of organic chemical (ppm level or less) in the region where Henry's law is applicable, the activity coefficient is the activity coefficient at infinite dilution ($\gamma_i = \gamma_i^\infty$). Thus

$$f_i^{liq} = \gamma_i^\infty\, x_i\, P_i^{SAT} \qquad \text{(B-6)}$$

For the liquid phase, the fugacity of the component is given by Henry's law that is applicable at very small concentration. The equation is

$$f_i^{liq} = H_i\, x_i \qquad (x_i << 1) \qquad \text{(B-7)}$$

Substitution of Equation (B-6) into Equation (B-7) yields

$$\gamma_i^\infty\, x_i\, P_i^{SAT} = H_i\, x_i \qquad \text{(B-8)}$$

Solving for Henry's law constant yields the following equation which is applicable to organic chemicals which are liquids at ambient conditions (25 C, 1 atm) and have total solubility in water:

$$H_i = \gamma_i^\infty\, P_i^{SAT} \qquad \text{(B-9)}$$

where H_i = Henry's law constant, atm/mol fraction
γ_i^{∞} = activity coefficient at infinite dilution
P_i^{SAT} = vapor pressure of organic chemical, atm

GASES

For organic chemicals that are gases at ambient conditions, there are two phases when the organic chemical is in contact with water. These are vapor and liquid phases. Such a two-phase system consisting of vapor and liquid is shown in Fig. B-1b. At equilibrium, the fugacity of the component in each phase is given by

$$f_i^{vap} = f_i^{liq} \tag{B-10}$$

For the vapor phase, the fugacity of the organic chemical is

$$f_i^{vap} = y_i \, P_t \tag{B-11}$$

Substitution of $y_i = 1\text{-}y_{H2O}$ and $P_t = 1$ atm into the equation yields

$$f_i^{vap} = 1\text{-}y_{H2O} \tag{B-12}$$

For the liquid phase, the fugacity of the component is given by Henry's law that is applicable at very small concentration. The equation is

$$f_i^{liq} = H_i \, x_i \qquad (x_i<<1) \tag{B-13}$$

Substitution of Equations (B-12) and (B-13) into Equation (B-10) yields

$$1\text{-}y_{H2O} = H_i \, x_i \tag{B-14}$$

Solving for Henry's law constant yields the following equation which is applicable to organic chemicals which are gases at ambient conditions (25 C, 1 atm):

$$H_i = (1\text{-}y_{H2O}) \, / \, x_i \tag{B-15}$$

where H_i = Henry's law constant, atm/mol fraction
x_i = solubility of organic chemical in water, mol fraction
y_{H2O} = mol fraction of water in vapor phase at ambient conditions (at 25 C, $y_{H2O} \approx 0.03117$)