

## AIR-WATER PARTITIONING: HENRY'S LAW

The transfer of a chemical compound between the atmosphere and bodies of water is one of the key processes affecting the transport of many organic compounds in the environment (1). This air-water distribution ratio ( $K_{aw}$ ) is also referred to as the Henry's Law constant  $K_H$ . The Henry's Law constant  $K_H$  can be approximated as the ratio of a compound's abundance in the gas phase to that in the aqueous phase at equilibrium.

$$X_{(aq)} \rightleftharpoons X_{(g)}$$

$$K_H = \frac{P_i}{C_w} \text{ atm.L.mol}^{-1}$$

where  $P_i$  is the partial pressure of the gas phase of the chemical and  $C_w$  is its molar concentration in water. Note that Henry's Law constant can be defined for the reverse reaction, which can lead to confusion. Tabulated  $K_H$  values have been reported in units of  $\text{Pa M}^{-1}$  and  $\text{atm m}^3 \text{mol}^{-1}$ . Some texts define the reaction in the opposite direction, in which case the units appear as  $\text{M atm}^{-1}$ .  $K_{aw}$  (also referred to as  $K_H'$ ) is defined in terms of a unitless ratio of concentrations. When in doubt, check the units!

Given that for most organic solutes of moderate or sparing solubility, the activity coefficient at infinite dilution in water is roughly equivalent to that in a saturated solution,

$$\gamma_w^\infty \sim \gamma_w^{\text{sat}}$$

we can approximate  $K_H$  by  $K_H^{\text{sat}}$ .

$$K_H \approx K_H^{\text{sat}} = \frac{P^\circ}{C_w^{\text{sat}}}$$

where  $P^\circ$  is for the liquid state (subcooled or superheated for solids and gases, respectively).

Since,

$$C_w^{\text{sat}} = \frac{1}{\gamma_w^{\text{sat}} \bar{V}_{\text{H}_2\text{O}}}$$

we can also write;

$$K_H = \bar{V}_{\text{H}_2\text{O}} \gamma_w^{\text{sat}} P^\circ \text{ (L) [dimensions of pressure} \times \text{volume} \times \text{mols}^{-1}\text{]}$$

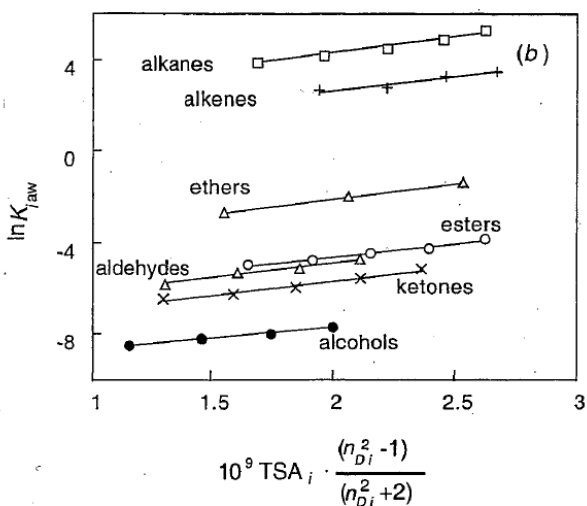
It will also be convenient for us to express the Henry's Law constant as a dimensionless  $K_{aw}$  value, and

it can be shown that

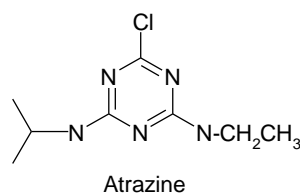
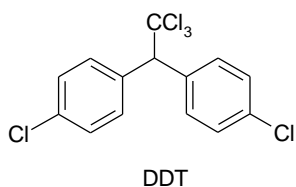
$$K_{aw} \text{ (dimensionless)} = \frac{K_H}{RT}$$

where the units used for  $R$  – the universal gas constant must be consistent with the units for  $K_H$  (i.e., if  $K_H$  is given in  $\text{atm L mol}^{-1}$ , then use  $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ ; if  $K_H$  is given in SI units of  $\text{Pa m}^3 \text{mol}^{-1}$ , then use  $R = 8.314 \text{ Pa m}^3 \text{mol}^{-1} \text{ K}^{-1}$ .)

Although both  $P^{\circ}(L)$  and  $C_w^{\text{sat}}$  decrease with molecular size, the water solubility is more sensitive to size increases due to the greater energy costs associated with cavity formation in water. Therefore, for a series of structurally related compounds, the magnitude of  $K_{\text{aw}}$  increases with size (i.e., molar volume or TSA). This is true because molecules that have similar functional groups will experience the same type of inter-molecular interactions. Increasing the size within the same functional group class, will result in a systematic increase in the dispersive forces. As can be seen in the figure below, alcohols have a much lower  $K_{\text{aw}}$  than alkanes due to the stronger solute:solute interactions (lower  $P^{\circ}$ ) and more favourable solute:solvent interactions (larger  $C_w^{\text{sat}}$ ). For molecules of similar size, alkenes are more polarizable than alkanes which results in more favourable solute:solute and solute:solvent induced dipole dispersive interactions, with the latter dominating the overall process. Monopolar molecules such as ethers, ester, ketones and aldehydes experience dipole – dipole interactions and can act as H-bond acceptor with the solvent, water.



If  $K_H$  has a relatively large value for a particular compound, it means it has a greater tendency to partition from the aqueous phase into the atmosphere. Consider the pesticides DDT and Atrazine both of which are very non-volatile with  $P^{\circ} \approx 1.3 \times 10^{-10}$  atm and  $P^{\circ} \approx 8.9 \times 10^{-10}$  atm at 25°C, respectively. Although Atrazine is about 7 times more volatile than DDT, it has much lower tendency to partition into the atmosphere from water. The  $K_H$  for atrazine is  $6.2 \times 10^{-6}$  atm.M<sup>-1</sup>, whereas that for DDT is  $9.5 \times 10^{-3}$  atm.M<sup>-1</sup> (both at 25°C). This is a direct result of the much lower water solubility of DDT ( $C_w^{\text{sat}} \approx 1.4 \times 10^{-8}$  M) as compared to  $1.5 \times 10^{-4}$  M for Atrazine. As a result, DDT has been observed to be widespread in the global environment at least in part due to atmospheric transport. Atrazine, on the other hand, tends to partition from air to water and is transported in the environment largely by the movement of water rather than the circulation of air.



## Effect of Temperature

Since,

$$\ln P^o = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + \text{constant}$$

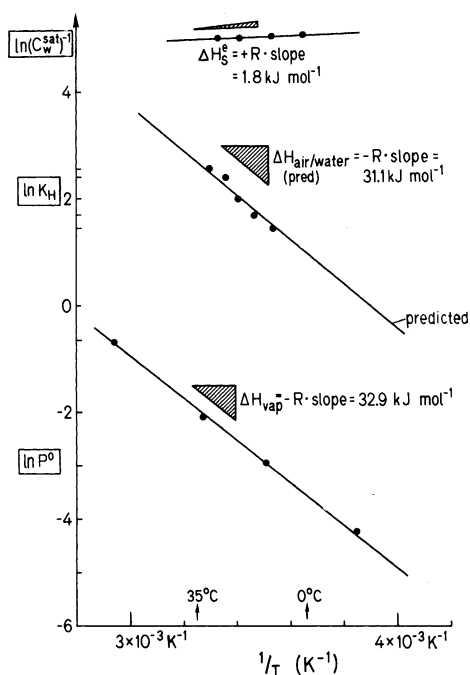
and

$$\ln C_w^{\text{sat}} = -\frac{\Delta H_s^e}{R} \left( \frac{1}{T} \right) + \text{constant}$$

we have;

$$\ln K_H^{\text{sat}} = -\frac{(\Delta H_{\text{vap}} - \Delta H_s^e)}{R} \left( \frac{1}{T} \right) + \text{constant} = -\frac{\Delta H_{\text{Henry}}}{R} \left( \frac{1}{T} \right) + \text{constant}$$

Hence, the temperature dependence of  $K_H$  for a given substance can be predicted with a knowledge of  $\Delta H_{\text{vap}}$  and  $\Delta H_s^e$ . Similar results are obtained for gaseous and solid compounds, making the necessary adjustments for the enthalpy of sublimation and fusion (melting) for solids and the enthalpy condensation for gases. The heat of vapourization of an organic liquid is positive and increases with molecular size and increasing polarity. The excess heat of solution ( $\Delta H_s^e$ ) is generally smaller. Hence, the effect of temperature on the magnitude of  $K_H$  is similar to that on the vapour pressure of the liquid compound. In other words, the dependence of the vapour pressure dominates over that of its water solubility and  $K_H$  generally decreases with decreasing temperature. The figure below shows a comparison of the observed temperature dependence of the Henry's Law constant for trichloroethylene with that predicted from the temperature variations of vapor pressure and water solubility.



## Salinity

The presence of salts in the aqueous phase will decrease the water solubility of organic solutes (increase the  $\gamma_w^{\text{sat}}$ ), but will obviously have no effect on the vapour pressure of the pure liquid. Hence,  $K_H$  values will increase with increasing salinity.

$$K_H^{\text{salt}} = K_H 10^{K^s [\text{salt}]_{\text{or}}}$$

Where  $K^s$  is the salt constant specific for a given organic compound. For seawater use  $[\text{salt}] \sim 0.5 \text{ M}$ . Recall the effect of salts on the water solubility;

$$C_{\text{salt}}^{\text{sat}} = C_w^{\text{sat}} 10^{-K^s [\text{salt}]_{\text{or}}}$$

## Methods of Determining $K_H$ Values

Experimental methods of determining  $K_H$  are usually based on analytical measurements of equilibrated air-water samples in a closed container. Expressing the fraction of solute in the gas phase as the ratio;

$$\text{fraction in gas phase} = \frac{C_g V_g}{C_g V_g + C_w V_w}$$

where  $V_g$  is the volume of the gas phase and  $V_w$  is the volume of the aqueous phase.

Substituting  $K_H' = C_g/C_w$  yields;

$$\text{fraction in gas phase} = \frac{K_H' V_g}{K_H' V_g + V_w} = \frac{V_g}{V_g + \frac{1}{K_H'} V_w}$$

Thus, if one determines the fraction of solute in the gas phase analytically,  $K_H'$  can be calculated with knowledge of the volumes of the aqueous and gas phases. Conversely, if one knows the value of  $K_H'$ , it is possible to calculate the fraction of solute in the gas and aqueous phases, respectively.

$K_H$  values can be difficult to measure directly, especially when  $C_w^{\text{sat}}$  is very low. Consequently, a number of estimation techniques have been proposed. A number of linear relationships between the  $K_H$  of a series of structurally related compounds and intrinsic properties such as total surface area or boiling points have been met with varying success. Another approach is to sum the contributions of structural units within a molecule to quantitatively predict the properties of the molecule as a whole. One such method introduced by Hine and Mookerjee considers the contribution of each bond type and is surprisingly simple to use. The assumption is that a specific structural unit will increase or decrease a compound's  $K_H$  by the same amount regardless of the actual compound. The contribution of each bond type is summed over the entire molecule such that;

$$\log K_H' = \sum a_i f_i$$

where  $a_i$  is the number of subunits of a particular type and  $f_i$  is the contributing factor for the particular subunit as refined and summarized by Meylan and Howard in the table below.

For example; the estimated value of  $K_H'$  using this approach for diethylether is;

$$\begin{aligned}\log K_H' &= 10(\text{C-H}) + 2(\text{C-O}) + 2(\text{C-C}) \\ \log K_H' &= 10(0.119) + 2(-1.09) + 2(-0.116) = -1.22\end{aligned}$$

$$\therefore K_H' = 10^{-1.22} = 0.0603$$

to convert this to  $K_H$  (in  $\text{atm M}^{-1}$ ) use;

$$\begin{aligned}K_H &= K_H' \times RT \\ &= 0.0603 (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (298 \text{ K}) \\ &= 1.47 \text{ atm M}^{-1}\end{aligned}$$

This compares reasonably well with the reported experimental value of  $1.62 \text{ atm M}^{-1}$  given the level of approximations involved. In general, these estimated values are good within a factor of  $\sim 2$  times the experimental values.

**Table 6.4** Bond Contributions for Estimation of  $\log K_{iaw}$  at 25°C <sup>a</sup>

Bond <sup>b</sup>	Contribution	Bond <sup>b</sup>	Contribution
C-H	+0.1197	C <sub>ar</sub> -OH	-0.5967 <sup>c</sup>
C-C	-0.1163	C <sub>ar</sub> -O	-0.3473 <sup>c</sup>
C-C <sub>ar</sub>	-0.1619	C <sub>ar</sub> -N <sub>ar</sub>	-1.6282
C-C <sub>d</sub>	-0.0635	C <sub>ar</sub> -S <sub>ar</sub>	-0.3739
C-C <sub>t</sub>	-0.5375	C <sub>ar</sub> -O <sub>ar</sub>	-0.2419
C-CO	-1.7057	C <sub>ar</sub> -S	-0.6345
C-N	-1.3001	C <sub>ar</sub> -N	-0.7304
C-O	-1.0855	C <sub>ar</sub> -I	-0.4806
C-S	-1.1056	C <sub>ar</sub> -F	+0.2214
C-Cl	-0.3335	C <sub>ar</sub> -C <sub>d</sub>	-0.4391
C-Br	-0.8187	C <sub>ar</sub> -CN	-1.8606
C-F	+0.4184	C <sub>ar</sub> -CO	-1.2387
C-I	-1.0074	C <sub>ar</sub> -Br	-0.2454
C-NO <sub>2</sub>	-3.1231	C <sub>ar</sub> -NO <sub>2</sub>	-2.2496
C-CN	-3.2624	CO-H	-1.2102
C-P	-0.7786	CO-O	-0.0714
C=S	+0.0460	CO-N	-2.4261
C <sub>d</sub> -H	+0.1005	CO-CO	-2.4000
C <sub>d</sub> =C <sub>d</sub>	-0.0000 <sup>d</sup>	O-H	-3.2318
C <sub>d</sub> -C <sub>d</sub>	-0.0997	O-P	-0.3930
C <sub>d</sub> -CO	-1.9260	O-O	+0.4036
C <sub>d</sub> -Cl	-0.0426	O=P	-1.6334
C <sub>d</sub> -CN	-2.5514	N-H	-1.2835
C <sub>d</sub> -O	-0.2051	N-N	-1.0956 <sup>e</sup>
C <sub>d</sub> -F	+0.3824	N=O	-1.0956 <sup>e</sup>
C <sub>t</sub> -H	-0.0040	N=N	-0.1374
C <sub>t</sub> ≡C <sub>t</sub>	-0.0000 <sup>d</sup>	S-H	-0.2247
C <sub>ar</sub> -H	+0.1543	S-S	+0.1891
C <sub>ar</sub> -C <sub>ar</sub>	-0.2638 <sup>f</sup>	S-P	-0.6334
C <sub>ar</sub> -C <sub>ar</sub>	-0.1490 <sup>g</sup>	S=P	+1.0317
C <sub>ar</sub> -Cl	+0.0241		

(1) *Environmental Organic Chemistry, 2 nd Ed.*, R.P. Schwarzenbach; P.M. Gschwend; D.M. Imoden, J. Wiley and Sons, **2004**.