AIR-WATER PARTITIONING: HENRY'S LAW

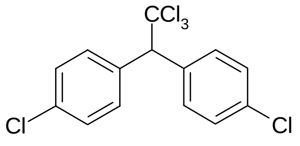
The transfer between the atmosphere and bodies of water is one of the key processes affecting the transport of many organic compounds in the environment (*1*). For neutral compounds, at dilute solution concentrations in pure water, the air-water distribution ratio is referred to as the Henry's Law constant K_H. For real aqueous solutions (i.e., solutions that contain many other chemical species), we use the term "air-water distribution ratio" which, for practical purposes, we approximate by the Henry's Law constant. 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.

$$X_{(aq)} \quad ==== \quad X_{(g)}$$

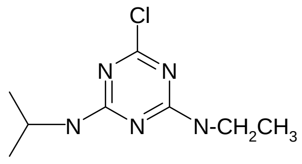
$$K_H = \frac{P_i}{C_w} \text{ atm.L.mol}^{-1}$$

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 has been defined in other terms, which can introduce confusion and caution should be used to check the units. K_H' is defined in terms of a unitless ratio of concentrations. Tabulated K_H values have been reported in units of Pa M^{-1} and atm m^3 mol^{-1}. Some texts define the reaction in the opposite direction, in which case the units appear as M atm^{-1}.

If K_H has a relatively large value for a particular compound, it means it has a large tendency to escape from the water phase and enter the atmosphere. For example, although the pesticide, DDT is essentially nonvolatile ($P° \approx 1.3 \times 10^{-10}$ atm at 25°C) its water solubility is also very small ($C_w^{sat} \approx 1.4 \times 10^{-8}$ M at 25°C). As a result a small quantity will be volatilized and this accounts for the widespread detection of DDT in environments far from the sites where it was applied ($K_H \approx 9.5 \times 10^{-3}$ atm.M^{-1} at 25°C). Another heavily applied chemical, the herbicide atrazine, is a little more volatile than DDT ($P° \approx 8.9 \times 10^{-10}$ atm at 25°C), but is far more soluble ($C_w^{sat} \approx 1.5 \times 10^{-4}$ M at 25°C), so its tendency to enter the atmosphere is negligible ($K_H \approx 6.2 \times 10^{-6}$ atm.M^{-1} at 25°C).



DDT



Atrazine

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

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

and we can approximate K_H by K_H^{sat}.

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

where P^o is for the liquid state (subcooled or superheated for solids and gases, respectively).
Since,

$$C_w^{sat} = \frac{1}{\gamma_w^{sat}\, \overline{V}_{H2O}}$$

we can also write;

$$K_H = \overline{V}_{H2O}\, \gamma_w^{sat}\, P^o(L)$$

Temperature

Since,

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

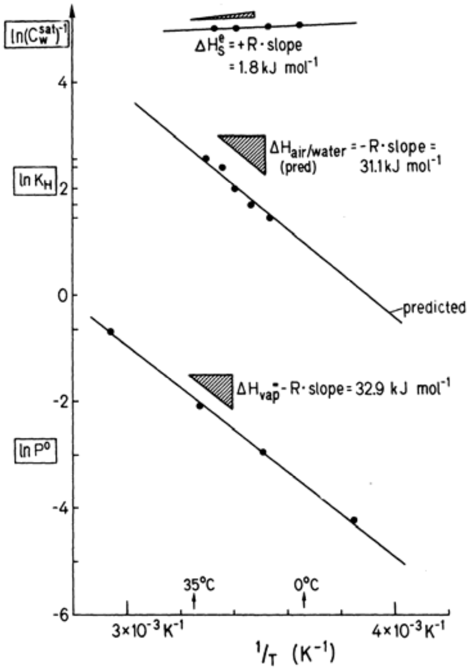
and

$$\ln C_{w}^{sat} = -\frac{\Delta H_{s}^{e}}{R}\left(\frac{1}{T}\right) + \text{constant}$$

we have;

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

The same result is obtained for gaseous and solid compounds. The temperature dependence of K_H can be predicted with a knowledge of ΔH_{vap} and ΔH_s^e. In general, the heat of vapourization of an organic liquid is positive and increases with molecular size and increasing polarity. The excess heat of solution (ΔH_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 it's 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 solubility.



Salinity

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

$$K_{H}^{salt} = K_{H}\, 10^{K^{s}\,[salt]_{tot}}$$

Where K^s is the salt constant specific for a given organic compound.

Recall the effect of salts on the water solubility;

$$C_{salt}^{sat} = C_{w}^{sat}\ 10^{-K^{s}\,[salt]_{tot}}$$

For seawater use [salt] ~ 0.5 M

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.

K_H values can be difficult to measure directly, especially when C_w^{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 considers the contribution of each bond type and is surprisingly simply and was introduced by Hine and Mookerjee. The idea 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;

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

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;

$\log K_H' = 10(C\text{-}H) + 2(C\text{-}O) + 2(C\text{-}C)$
$\log K_H' = 10(0.119) + 2(-1.09) + 2(-0.116) = -1.22$
$\therefore\ K_H' = 10^{-1.22} = 0.0603$
to convert this to K_H (in atm M^{-1}) use;
$K_H = K_H' \times RT$
$= 0.0603\ (0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})\ (298\ \text{K})$
$= 1.47\ \text{atm}\ M^{-1}$

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

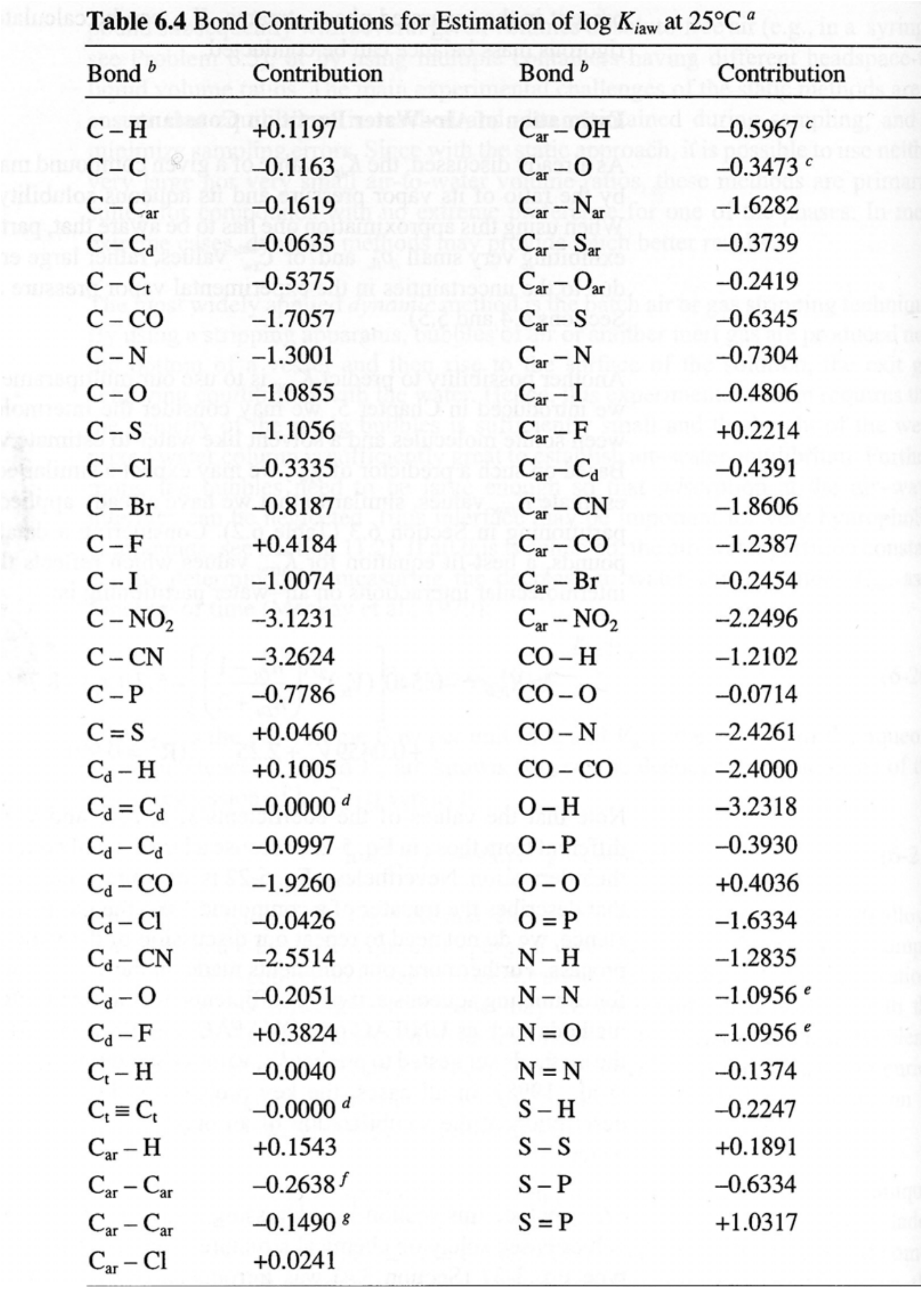


Table 6.4 Bond Contributions for Estimation of log K_{iaw} at 25°C [a]

Bond [b]	Contribution	Bond [b]	Contribution
$C-H$	+0.1197	$C_{ar}-OH$	−0.5967 [c]
$C-C$	−0.1163	$C_{ar}-O$	−0.3473 [c]
$C-C_{ar}$	−0.1619	$C_{ar}-N_{ar}$	−1.6282
$C-C_d$	−0.0635	$C_{ar}-S_{ar}$	−0.3739
$C-C_t$	−0.5375	$C_{ar}-O_{ar}$	−0.2419
$C-CO$	−1.7057	$C_{ar}-S$	−0.6345
$C-N$	−1.3001	$C_{ar}-N$	−0.7304
$C-O$	−1.0855	$C_{ar}-I$	−0.4806
$C-S$	−1.1056	$C_{ar}-F$	+0.2214
$C-Cl$	−0.3335	$C_{ar}-C_d$	−0.4391
$C-Br$	−0.8187	$C_{ar}-CN$	−1.8606
$C-F$	+0.4184	$C_{ar}-CO$	−1.2387
$C-I$	−1.0074	$C_{ar}-Br$	−0.2454
$C-NO_2$	−3.1231	$C_{ar}-NO_2$	−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_d-H	+0.1005	$CO-CO$	−2.4000
$C_d=C_d$	−0.0000 [d]	$O-H$	−3.2318
C_d-C_d	−0.0997	$O-P$	−0.3930
C_d-CO	−1.9260	$O-O$	+0.4036
C_d-Cl	−0.0426	$O=P$	−1.6334
C_d-CN	−2.5514	$N-H$	−1.2835
C_d-O	−0.2051	$N-N$	−1.0956 [e]
C_d-F	+0.3824	$N=O$	−1.0956 [e]
C_t-H	−0.0040	$N=N$	−0.1374
$C_t\equiv C_t$	−0.0000 [d]	$S-H$	−0.2247
$C_{ar}-H$	+0.1543	$S-S$	+0.1891
$C_{ar}-C_{ar}$	−0.2638 [f]	$S-P$	−0.6334
$C_{ar}-C_{ar}$	−0.1490 [g]	$S=P$	+1.0317
$C_{ar}-Cl$	+0.0241		

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