

Addendum I: Henry's Law Constants of OH and HO₂

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The Henry's law type constants of OH and HO₂ have not been experimentally determined for obvious reasons: it is extremely difficult to measure the concentrations of these reactive species in either the gas phase or the aqueous phase, let alone simultaneously in both phases. At a more fundamental level, because these radicals react rapidly in both phases, e.g. [1–3], compared with mass-transfer rates characterizing typical laboratory multi-phase systems, the gas–liquid equilibrium which is necessary for such measurements to be feasible is typically not attainable. Consequently, the Henry's law constants of these radicals are traditionally evaluated from the free energy of solution, $\Delta_{\text{sol}}G^\circ(\text{X})$ accompanying the process of transferring a molecule X from the gas phase, denoted g, to the aqueous phase, a, i.e.



using the equation

$$\Delta_{\text{sol}}G^\circ(\text{X}) = -RT \ln k_H \quad (9.11)$$

$\Delta_{\text{sol}}G^\circ(\text{X})$ is defined as

$$\Delta_{\text{sol}}G^\circ(\text{X}) = \Delta_f G^\circ(\text{X})_a - \Delta_f G^\circ(\text{X})_g \quad (9.12)$$

where the free energies of formation of X in the gas phase and in the aqueous phase are typically evaluated using thermochemical cycles.

It should be pointed out that, because the Henry's law constant determined in the way described above is a function of the difference between two comparable numbers in the exponent, the uncertainty is therefore generally sizable. A small uncertainty of 0.8 kJ mol⁻¹ in the individual quantity would correspond to ~50 % uncertainty in the value of k_H . Since a typical combined uncertainty is rarely

