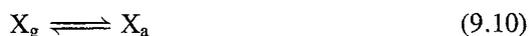


Addendum I: Henry's Law Constants of OH and HO₂

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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

smaller than 2.1 kJ mol⁻¹ the Henry's law constant evaluated in this fashion cannot be expected to have an uncertainty smaller than a factor of 2.

Finally, it is noted that both of these radicals undergo acid-base dissociation in aqueous solution. Consequently, the effective Henry's law solubilities, k_H^* , of these species depend on their pK_a and pH of the solution, i.e.

$$k_H^* = k_H(1 + K_a/[H^+]) \quad (9.13)$$

The pK_a values of HO₂ and OH have been determined as 4.9 [4] and 11.9 [5], respectively. The heats of ionization of HO₂ and OH were determined as 0 and 42 ± 8 kJ mol⁻¹ [6]. Later, Bielski [7] recommended a value of 4.69 for the pK_a of HO₂. For liquid water typically encountered in the environment, such as cloud, rain and seawater, the pH falls in the range between ~ 3 and ~ 8.5 , encompassing the pK_a of HO₂. Consequently, the effective Henry's law constant of HO₂ must be considered for HO₂. However, because of the large pK_a of OH compared with the aforementioned pH range, its effective Henry's law solubility is not expected to be affected by the solution pH of these aqueous media.

1 OH [CAS 3352-57-6]

Values of thermodynamic properties of OH in aqueous solution are listed in Table 9.43. Values for OH in the gas phase are listed in Table 9.44. The Henry's law constant of OH has been estimated by various investigators and the values range from 25 to 1×10^5 mol dm⁻³ bar⁻¹ [18]. While the high values were simply assumed by Chameides [19], Jacob [20] adhered to a much smaller value of 25 mol dm⁻³ bar⁻¹ (298 K), as did Schwartz [21], based on Schwarz and Dodson [11]. However, it is recognized that the large discrepancies in the value of Henry's law constant of OH have little substantive impact on a model's ability to describe the atmospheric chemistry and distribution of this important species, as stated for example by Lelieveld and Crutzen [18].

Table 9.43 Thermodynamic properties of aqueous OH

Quantity	Value	Ref.
$\Delta_f G_a^\circ / \text{kJ mol}^{-1}$	13.39	8,9
	19.00	10
	25.10	11
	26.82	12
	35.69	13
$\Delta_f H_a^\circ / \text{kJ mol}^{-1}$	7.1	14
	-4.2	10
$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$	96	14
$\Delta_{\text{sol}} G^\circ / \text{kJ mol}^{-1}$	-10.0	11
	-20.9	8
pK_a	11.9	15

Table 9.44 Thermodynamic properties of gaseous OH

Quantity	Value	Ref.
$\Delta_f G_g^\circ/\text{kJ mol}^{-1}$	34.31	16
$\Delta_f H_g^\circ/\text{kJ mol}^{-1}$	38.99	16
	44.4	17
	37.28	17
	39.12	17
	41.8	17

Table 9.45 Gibbs energy of solution, $\Delta_{\text{sol}} G^\circ$

Species	Value/kJ mol ⁻¹	Ref.
HO	-25	22
	-15.5	10
	-5.0	23
	-8.4	24

The value of $\Delta_{\text{sol}} G^\circ$ for OH was estimated by Koppenol and Liebman [8] to be -21 kJ mol^{-1} . This corresponds to a Henry's law constant of $4.6 \times 10^3 \text{ mol dm}^{-3} \text{ bar}^{-1}$. The values of $\Delta_{\text{sol}} G^\circ$ which have appeared in the literature range from 17.6 to -25 kJ mol^{-1} (Table 9.45), and would result in Henry's law constant values from 8 to $2.5 \times 10^4 \text{ mol dm}^{-3} \text{ bar}^{-1}$. However, using the average value of $\Delta_f G_g^\circ = 34.64 \pm 3.51 \text{ kJ mol}^{-1}$ and $\Delta_f G_a^\circ = 21.09 \pm 6.11 \text{ kJ mol}^{-1}$ results in a Henry's law constant of $237 \text{ mol dm}^{-3} \text{ bar}^{-1}$ for HO, with a large uncertainty of 15 to 4×10^4 . This is of little consequence in the development of models of the atmospheric chemistry of HO.

2 HO₂ [CAS 3170-83-0]

Values of thermodynamic properties of HO₂ in aqueous solution are listed in Table 9.46. The first explicit evaluation of the Henry's law constant of HO₂

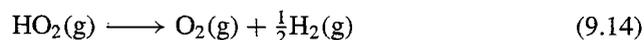
Table 9.46 Thermodynamic properties of aqueous HO₂

Quantity	Value	Ref.
$\Delta_f G_a^\circ/\text{kJ mol}^{-1}$	5.06 ± 0.84	25
$\Delta_f H_a^\circ/\text{kJ mol}^{-1}$	-36.0 ± 4.2	14
$S^\circ/\text{J mol}^{-1} \text{ K}^{-1}$	138 ± 4	14
$\Delta_{\text{sol}} G_a^\circ/\text{kJ mol}^{-1}$	$-356 (\text{O}_2^-)$	26
$\text{p}K_a$	4.8 ± 0.1	3

Table 9.47 Thermodynamic properties of HO₂(g)

Quantity	Value	Ref.
$\Delta_f G_g^\circ/\text{kJ mol}^{-1}$	22.6 ± 2.5	29
	14.43	16
	26.8	30
$\Delta_f H_g^\circ/\text{kJ mol}^{-1}$	10.5 ± 2.5	29
	2.1 ± 8.4	16
	$14.6 + 4.2/-2.1$	27
	14.6	31
	16.82 ± 2.51	32
	15.90 ± 5.02	28
	22.2	33
$T\Delta_f S_g^\circ/\text{kJ mol}^{-1}$	-12.30	29
$S^\circ/\text{J mol}^{-1} \text{K}^{-1}$	228.99	29

using a thermochemical cycle was given by Schwartz [25] as shown below.



A value of $1.2 \times 10^3 \text{ mol dm}^{-3} \text{ bar}^{-1}$ was recommended based on an estimated value of $5.06 \pm 0.84 \text{ kJ mol}^{-1}$ for $\Delta_f G^\circ(\text{HO}_2)_a$ in combination with a $\Delta_f G^\circ(\text{HO}_2)_g = 22.6 \text{ kJ mol}^{-1}$. It was also pointed out that, because of the uncertainty in the value of the enthalpy of formation of HO₂, $\Delta_f H_g^\circ$, which was used to deduce $\Delta G^\circ(\text{HO}_2)_g$, the value of $k_H(\text{HO}_2)$ may be as large as $6.7 \times 10^3 \text{ mol dm}^{-3} \text{ bar}^{-1}$ if $\Delta_f H_g^\circ = 14.6 \text{ kJ mol}^{-1}$ were used. The recommended value by Shum and Benson [27] for $\Delta_f H_g^\circ$ is $14.6(+4.2, -2.1) \text{ kJ mol}^{-1}$, contrasting with a JANAF value of $2.1 \pm 8.4 \text{ kJ mol}^{-1}$ [16]. Although Chameides [19] adopted a high value for $k_H(\text{HO}_2)$, i.e. $9 \times 10^3 \text{ mol dm}^{-3} \text{ bar}^{-1}$ (291 K), Jacob [20] adhered to an intermediate value of $4 \times 10^3 \text{ mol dm}^{-3} \text{ bar}^{-1}$ in a review of atmospheric heterogeneous chemistry.

Since the study of Shum and Benson [27], several additional values of $\Delta_f H_g^\circ$ have appeared in the literature. These values are compiled in Table 9.47. Fisher and Armentrout [28] compared their experimentally determined value, $15.9 \pm 5.0 \text{ kJ mol}^{-1}$, with the available data and found good agreement with both the value recommended by Shum and Benson [9] and that measured by Howard [29] (Table 9.47). In the case of the experimentally determined appearance energy of ion radicals, Holmes *et al.* [29] reported a value of 14.6 kJ mol^{-1} for $\Delta_f H^\circ(\text{HO}_2)$, in excellent agreement with the recommended value by Shum and Benson [27]. Later, Espinosa-Garcia [32] reported a theoretical value of $16.82 \pm 2.51 \text{ kJ mol}^{-1}$ and suggested that earlier calculations such as that of Sana *et al.* [34] may represent overestimates. Judging from the fairly consistent experimentally determined results and a downward trend in the calculated values which asymptotically

approach the experimental values, the value recommended for $\Delta_f H^\circ(\text{HO}_2)_g$ by Shum and Benson [27] is the most appropriate to use. With the use of the value $14.6 \pm 4.2 \text{ kJ mol}^{-1}$ for $\Delta_f H^\circ_g$ which leads to $\Delta_f G^\circ_g = 26.94 \pm 4.18 \text{ kJ mol}^{-1}$ and $\Delta_f G^\circ_a = 5.06 \pm 0.84 \text{ kJ mol}^{-1}$ evaluated by Schwartz [25], the Henry's law constant of HO₂ is estimated to be $6.8 \times 10^3 \text{ mol dm}^{-3} \text{ bar}^{-1}$. However, in view of the fairly large uncertainties of the thermodynamic values involved in the calculation, 1.3×10^3 to $3.7 \times 10^4 \text{ mol dm}^{-3} \text{ bar}^{-1}$ may be used as bounds.

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