

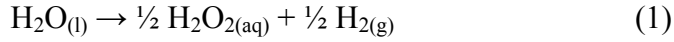
Supporting information for “Experimental and Thermodynamic Viewpoints on Claims of a Spontaneous H₂O₂ Formation at the Air-Water Interface”

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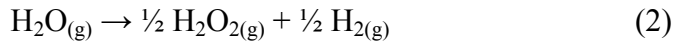
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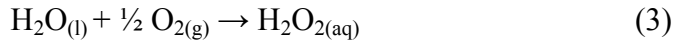
1. Standard Gibbs free energies of some reactions for H₂O₂ formation in water solution and gas phase.



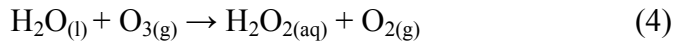
$$\Delta G^\circ = \frac{1}{2}(\Delta G_{\text{H}_2\text{O}_2, \text{aq}}^\circ + \Delta G_{\text{H}_2, \text{g}}^\circ) - \Delta G_{\text{H}_2\text{O}, l}^\circ = \frac{1}{2}(-134.1 \text{ kJ} \cdot \text{mol}^{-1} + 0 \text{ kJ} \cdot \text{mol}^{-1}) - (-237.1 \text{ kJ} \cdot \text{mol}^{-1}) = 170.0 \text{ kJ} \cdot \text{mol}^{-1} = 40.7 \text{ kcal} \cdot \text{mol}^{-1}$$



$$\Delta G^\circ = \frac{1}{2}(\Delta G_{\text{H}_2\text{O}_2, \text{g}}^\circ + \Delta G_{\text{H}_2, \text{g}}^\circ) - \Delta G_{\text{H}_2\text{O}, \text{g}}^\circ = \frac{1}{2}(-105.6 \text{ kJ} \cdot \text{mol}^{-1} + 0 \text{ kJ} \cdot \text{mol}^{-1}) - (-228.6 \text{ kJ} \cdot \text{mol}^{-1}) = 175.8 \text{ kJ} \cdot \text{mol}^{-1} = 42.1 \text{ kcal} \cdot \text{mol}^{-1}$$



$$\Delta G^\circ = \Delta G_{\text{H}_2\text{O}_2, \text{aq}}^\circ - \left(\Delta G_{\text{H}_2\text{O}, l}^\circ + \frac{1}{2} \Delta G_{\text{O}_2, \text{g}}^\circ \right) = -134.1 \text{ kJ} \cdot \text{mol}^{-1} - \left(-237.1 \text{ kJ} \cdot \text{mol}^{-1} + \frac{1}{2} \times 0 \text{ kJ} \cdot \text{mol}^{-1} \right) = 103.0 \text{ kJ} \cdot \text{mol}^{-1} = 24.6 \text{ kcal} \cdot \text{mol}^{-1}$$



$$\Delta G^\circ = (\Delta G_{\text{H}_2\text{O}_2, \text{aq}}^\circ + \Delta G_{\text{O}_2, \text{g}}^\circ) - \left(\Delta G_{\text{H}_2\text{O}, l}^\circ + \frac{1}{2} \Delta G_{\text{O}_3, \text{g}}^\circ \right) = (-134.1 \text{ kJ} \cdot \text{mol}^{-1} + 0 \text{ kJ} \cdot \text{mol}^{-1}) - ((-237.1 \text{ kJ} \cdot \text{mol}^{-1}) + 163.2 \text{ kJ} \cdot \text{mol}^{-1}) = -60.2 \text{ kJ} \cdot \text{mol}^{-1} = -14.4 \text{ kcal} \cdot \text{mol}^{-1}$$

All the above data were extracted from Ref. 1

2. Thermodynamic quantities of chemical species that may be relevant to H₂O₂ formation

Table S1. Thermodynamic quantities of chemical species that could be relevant to hydrogen peroxide formation

| Chemical species | | H ₂ O | •OH | H ₂ O ₂ | H ₂ | H ₃ O ⁺ | OH ⁻ | e ⁻ | |
|---|---------------|-----------------------------|--|--|--|---|---|---|--|
| Enthalpy of Formation (ΔH_f° , kJ·mol ⁻¹) | Gas phase | -241.8 ¹ | 39.0 ¹ | -136.3 ¹ | 0 | 584.2 ² | -143.6 ² | | |
| | Interface | | | | | | | | |
| | Bulk | -285.83 (l) ¹ | -0.8 ± 5.9 (aq) ³ | -187.8 (l) ¹ -191.2 (aq) ¹ | | 144.3 (aq) ⁴ | -230.0 (aq) ¹ | 277.4 (aq) ⁵ | |
| Gibbs Energy of Formation (ΔG_f° , kJ·mol ⁻¹) | Gas phase | -228.6 ¹ | 34.2 ¹ | -105.6 ¹ | 0 | 606.6 ² | -138.7 ² | | |
| | Interface | | | | | | | | |
| | Bulk | -237.1 (l) ¹ | 24.3 (aq) ³ | -120.4 (l) ¹ -134.1 (aq) ¹ | | 183.9 (aq) ⁴ | -157.3 (aq) ¹ | 276.9 (aq) ⁵ | |
| Entropy (S° , J·K ⁻¹ ·mol ⁻¹) | Gas phase | 188.8 ¹ | 183.6 ¹ | 232.7 ¹ | 130.7 ¹ | 192.3 ² | 172.5 ² | | |
| | Interface | | | | | | | | |
| | Bulk | 69.9 ¹ | | 109.6 (l) ¹ 143.9 (aq) ¹ | | | -10.9 (aq) ¹ | 66.9 (aq) ⁵ | |
| Solvation Energy* (kJ·mol ⁻¹) | Gas phase | | | | | | | | |
| | Interface | | -17.3 (cal) ⁶ -16.74 (cal) ⁷ | -43.9 (cal) ⁸ | | -424.7 (cal) ⁹ | -440.6 (stabilized by 1 k_bT) ¹⁰ | -154.4 (VBE, exp) ¹¹ | |
| | Bulk | | -29.8 (aq, cal) ¹² -26.4 (aq, exp) ¹³ | -13.4 (aq, cal) ⁶ -12.5 (l, cal) ⁷ -16.32 (l, exp) ⁷ | -41.8 (aq, cal) ⁸ -36.6 (aq, exp) ⁸ | 9.2 (cal) ¹⁴ 9.79 (exp) ¹⁵ | 651.0 (aq, con, cal) ¹⁶ -461.5 (aq, abs, cal) ¹⁶ -439.3 (aq, cal) ⁹ | -1550.6 (aq, con, cal) ¹⁶ -438.1 (aq, abs, cal) ¹⁶ | -164.8 (exp) ¹⁷ -148.5 (cal) ¹⁸ -318.4 (VBE, exp) ¹¹ |
| | | | | | | | | | |
| Henry's Law Constants (H_s^{cp} , mol ⁻¹ ·m ³ ·Pa ⁻¹) | Water solvent | | 0.38 ¹⁹ | 910 ¹⁹ | 7.80×10 ⁻⁶ ¹⁹ | | | | |

| | | | | | | | |
|----------------------------------|-----------|--|---|--|---|--|--|
| Ionization Energy (eV) | Gas phase | 12.61 (exp) ¹ | 13.02 (cal) ²⁰ 13.02 (exp) ²¹ | 10.64 (cal) ²² 10.65 (exp) ²² | 15.32 (cal) ²³ 15.43 (exp) ¹ | 1.90 (VDE, exp) ²⁴ | |
| | Interface | 10.30 (cal) ₂₅ | | | | | |
| | Bulk | ~10 (exp) ²⁵ 10.55 (cal) ²⁵ | | 10.54 (aq, exp) ²⁶ | 14.5 (cal) ²⁷ | 9.20 (exp) ²⁷ 9.70 (cal) ²⁷ | 3.3 (VBE, cal) ²⁸ 3.3-3.7 (VBE, exp) ²⁹ |
| Standard Reduction Potential (V) | Gas phase | | | | | | |
| | Interface | | | | | | |
| | Bulk | -0.8 (H ₂ O/H ₂ , OH ⁻) ¹ | 2.7 (·OH, H ⁺ /H ₂ O) ³⁰ 1.9 (·OH/OH ⁻) ₃₀ | 0.8 (H ₂ O ₂ , H ⁺ /H ₂ O, ·OH) ³⁰ 1.8 (H ₂ O ₂ , H ⁺ /H ₂ O) ₁ | | | -2.7 (aq/e _{aq} ⁻) ³⁰ |

*The absolute and conventional solvation free energies are presented. The absolute value of a single ion cannot be measured, the conventional value is therefore often tabulated by arbitrarily setting the free energy of solvation of the proton equal to zero.¹⁶

Note. water solvent unless specified, l – liquid, aq – aqueous, VBE – vertical binding energy, VDE – vertical detachment energy, abs – absolute, cal – calculated.

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