Unit 16

Aqueous phase chemistry

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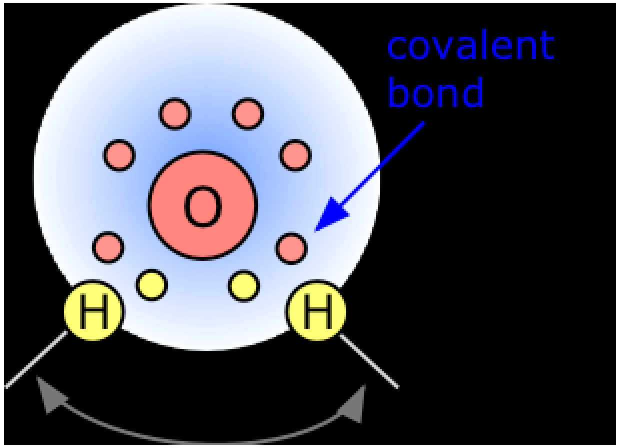
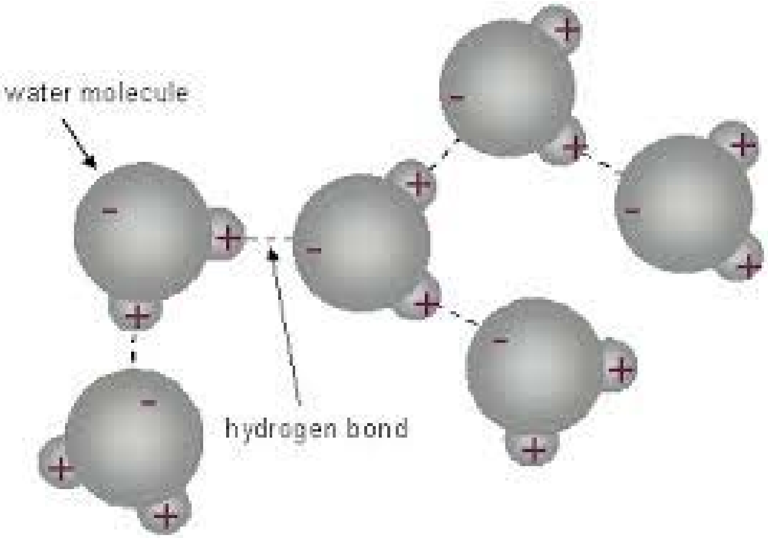
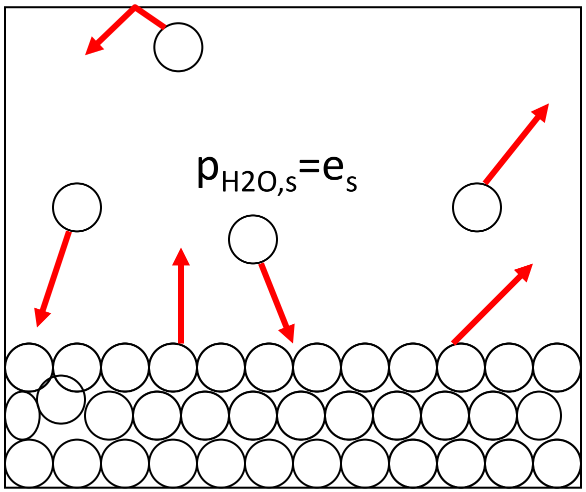
Forces

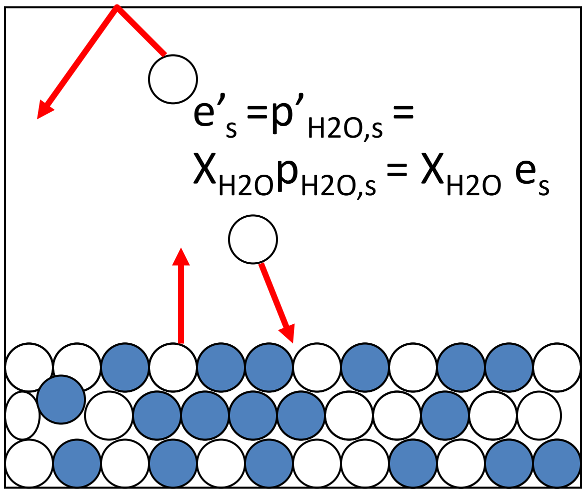




Dissolution of gases



Water saturation vapor pressure over pure liquid water surface



Water saturation vapor pressure over aqueous solution of water mixing ratio X_{H2O}

White: water molecules
Blue: solute molecules

$$X_{H2O}=e'_s / e_s=p'_{H2O,s} / p_{H2O,s}=RH/100$$

Solubility

$$A(g) \rightleftharpoons A(aq)$$

$$A(g) + H_2O \rightleftharpoons A \cdot H_2O$$

$$[A \cdot H_2O] = k_H p_A$$

$$\frac{[A \cdot H_2O]}{[A(g)]} \frac{k_H p_g}{p_g/(R_c^* T)} = k_H R_c^* T = \hat{k}_H$$

$$\frac{d ln k_H}{dT} = \frac{\Delta H}{R_c^* T^2}$$

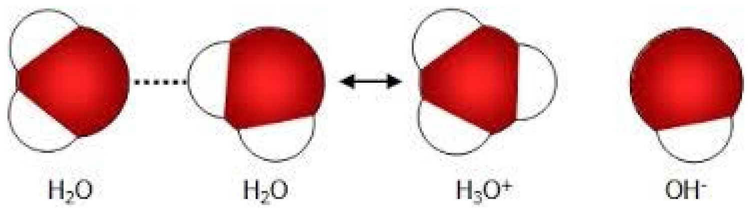
$$k_H(T_2) = k_H T_1 \exp\left(\frac{\Delta \overline{H_0}}{R_c^*}(\frac{1}{T_1} - \frac{1}{T_2})\right)$$

Ionization

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) = [H^+] + A^-(aq)$$

$[H_3O^+(aq)]=[H^+]$

$$k_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$



http://faculty.clintoncc.suny.edu/faculty/michael.gregory/files/bio%20101/bio%20101%20lectures/chemistry/ionization%20of%20water.png

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

$$k_b = \frac{[HA(aq)][OH^-(aq)]}{[A^-(aq)]}$$

$$k_w = k_a k_b = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]} \frac{[HA(aq)][OH^-(aq)]}{[A^-(aq)]}$$

$$= [H_3O^+(aq)][OH^-(aq)] = [H^+][OH^-]$$

pH-scale

$$H_2O \rightleftharpoons^{k'_w} H^+ + OH^-$$

$$k'_w = \frac{[H^+][OH]}{[H_2O]}$$

$$k_w = [H^+][OH^-] = 10^{-14} M^2$$

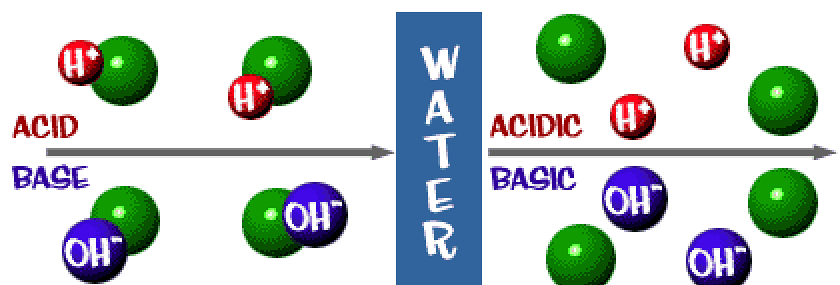
$$[H^+] = [OH^-]$$

$$[H^+] = \sqrt{10^{-14} M^2} = 10^{-7} M$$

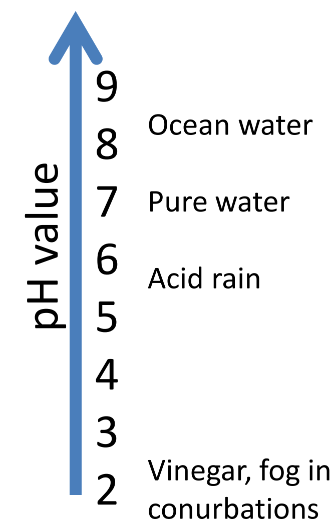
$$[H^+(aq)] > [OH^-(aq)]$$

$$[H^+(aq)] < [OH^-(aq)]$$

$$pH = -\log[H^+] = -\log[H_3O^+(aq)]$$

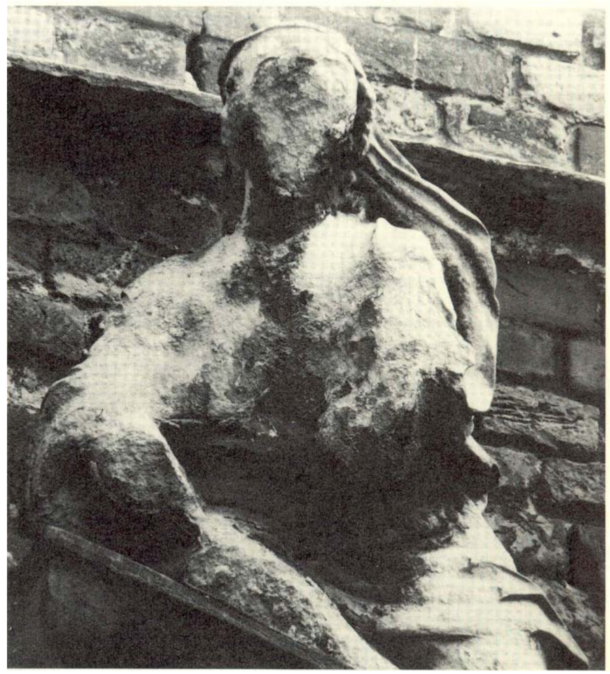


http://www.chem4kids.com/files/art/reaction_acidbase3.gif



Results of acid rain

Sandstone portal figure on Herten Castle
in the Rhein-Ruhr district, Germany
sculpted 1702; photographed in 1908

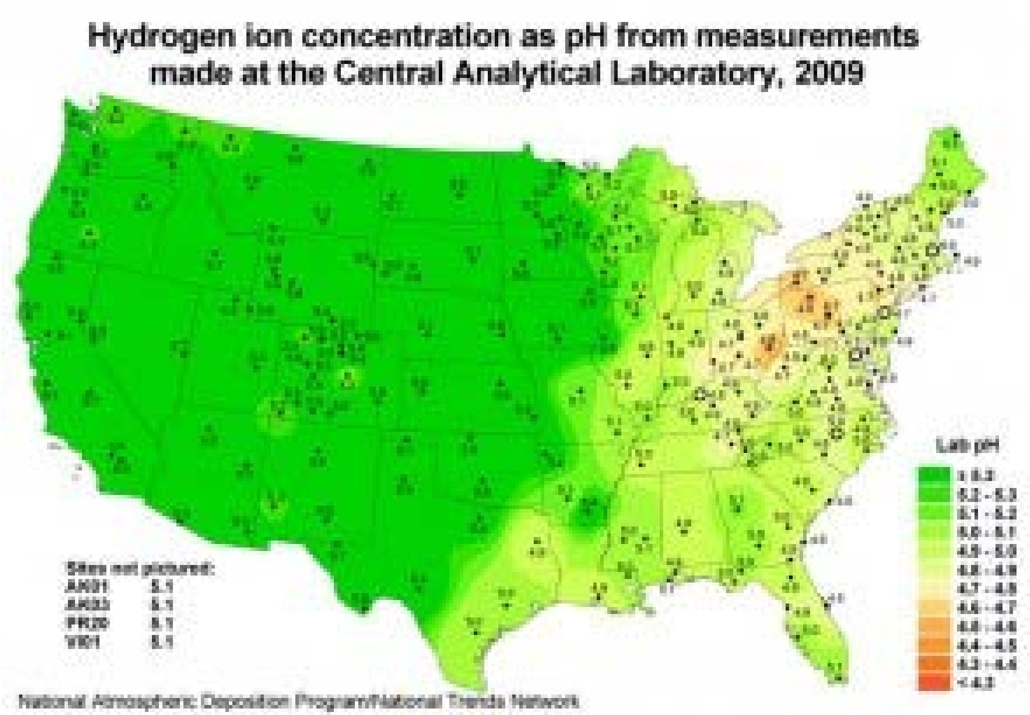


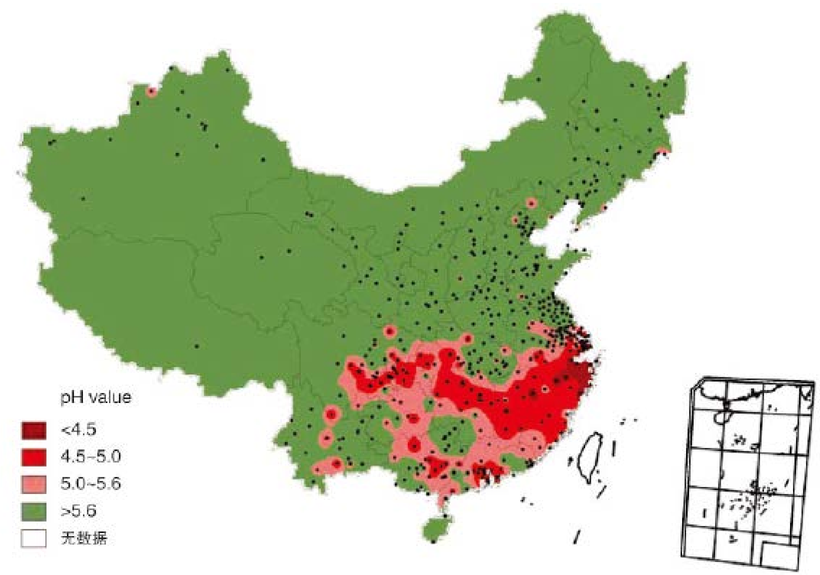
Same figure photographed in 1969

Forest dying due to acid rain

$$CaCO_3\text{ (solid)} \Leftrightarrow Ca^{2+}\text{ (aq)} + CO_3^{2-}\text{ (aq)}$$

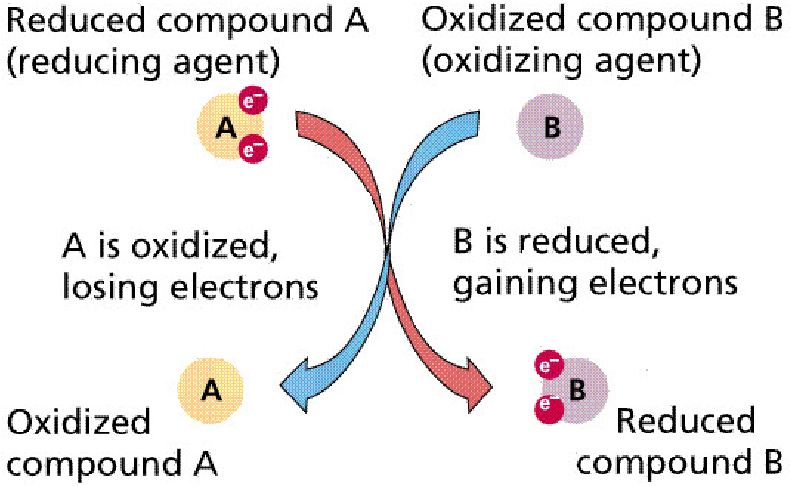
pH distributions





Acid-base equilibrium

$$k_{eff}(A) = k_H(A)\left(1 + \frac{k_1}{[B(aq)]^b} + \frac{k_2}{[C(aq)]^c} + \cdots\right)$$



http://isite.lps.org/sputnam/LHS_IB/IBChemistry/UNIT6Redox/IBCUnit6Redox.html

Aqueous phase reactions

$$SO_2(g) \rightleftharpoons SO_2(aq)$$

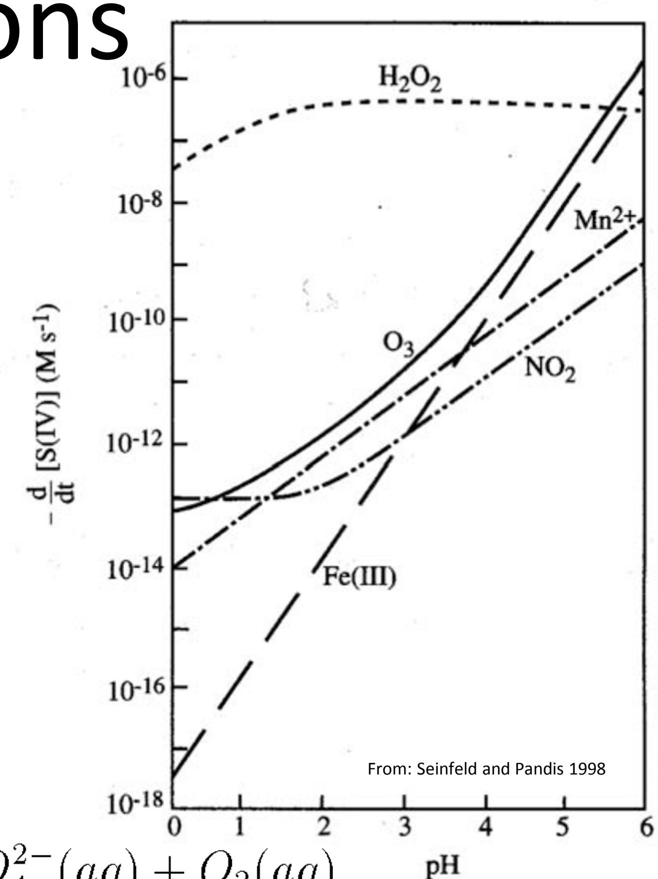
$$SO_2 + H_2O \rightarrow H^+ + HSO_3^-$$

$$2HSO_3^- + O_2 + M \rightarrow 2H^+ + 2SO_4^{2-} + M$$

$$HSO_3^-(aq) + H_2O_2(aq) \rightleftharpoons SO_2OOH^-(aq) + H_2O(aq)$$

$$SO_2OOH^-(aq) + H_3O^+(aq) \rightleftharpoons H_2SO_4(aq) + H_2O(aq)$$

$$-\frac{d[S(IV)]}{dt} = \frac{k[H_3O^+(aq)][H_2O_2(aq)][HSO_3^-(aq)]}{1 + K[H_3O^+(aq)]}$$



$$SO_2 \cdot H_2O(aq) + HSO_3^-(aq) + SO_3^{2-}(aq) + O_3(aq) \longrightarrow SO_4^{2-}(aq) + O_2(aq)$$

$$-\frac{d[S(IV)]}{dt} = (k_0[SO_2 \cdot H_2O(aq)] + k_1[HSO_3^-(aq)] + k_2[SO_3^{2-}])[O_3(aq)]$$

$$2HSO_3^-(aq) + O_2(aq) + 2H_2O(aq) \longrightarrow^{Fe^{3+}, Mn^{2+}} 2(SO_4^{2-}(aq) + H_3O^+(aq))$$

$$2NO_2(aq) + HSO_3^-(aq) + 4H_2O(aq) \longrightarrow 3H_3O^+(aq) + 2NO_2^-(aq) + SO_4^{2-}(aq)$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

References

Material shown here partly stems from:

- *www.atmos.uiuc.edu/courses/atmos348.../Atmos348Lecture17.pdf*
- *www.ees.ufl.edu/homepp/cywu/.../Equilibrium%20&%20Kinetics.ppt*
- http://ua.acd.ucar.edu/Presentations/lecture2.pdf
- http://www.atmos.uiuc.edu/courses/atmos348-sp04/documents/Atmos348Lecture5.pdf
- *www.authorstream.com/.../aSGuest8996-131504-smog-chemistry-project-science-technology-ppt-powerpoint/*