

Acids and bases



$$K_{\text{eq}} = \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]}$$

$$\log K_{\text{eq}} = \frac{\log [\text{A}^-]}{[\text{AH}]} + \log [\text{H}^+]$$

$$-\log [\text{H}^+] = -\log K_{\text{eq}} + \log \frac{[\text{A}^-]}{[\text{AH}]}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{AH}]} \quad \Delta G = \Delta G^\circ + \log \frac{\text{product}}{\text{reactant}}$$

$$\text{pH} - \text{pK}_a = \log \frac{[\text{A}^-]}{[\text{AH}]}$$

when pH = pK_a then [A⁻] = [AH]

For example if the pK = 7 = -log K_{eq} so log K_{eq} = -7

$$\Delta G^\circ = -RT \ln K_{\text{eq}} = -1.36 \text{ kcal/mol} \log K_{\text{eq}} = +9.52 \text{ kcal/mol}$$

At pH 7 (when [H⁺] = 10⁻⁷ molal) what is the equilibrium mixture of A⁻ and AH?

$$\Delta G = \Delta G^\circ + 1.36 \text{ kcal/mol} \cdot \log \frac{[\text{A}^-][10^{-7}]}{[\text{AH}]} = \Delta G^\circ + 1.36 \text{ kcal/mol} \cdot \log \frac{[\text{A}^-]}{[\text{AH}]} - \text{pH}$$

$$\text{at equil } \Delta G = 0 = \Delta G^\circ + 1.36 \log \frac{[\text{A}^-]}{[\text{AH}]} - 1.36 \text{ pH}$$

$$-\log \frac{[\text{A}^-]}{[\text{AH}]} = -(\Delta G^\circ / 1.36 - 7) = (9.52 / 1.36 - 7) = 0$$

$$\rightarrow \frac{[\text{A}^-]}{[\text{AH}]} = 1 \text{ at pK} = \text{pH}$$

$$\text{At pH 5} \quad -\log \frac{[\text{A}^-]}{[\text{AH}]} = (9.52 / 1.36 - 5) = 2; \rightarrow \log \frac{[\text{A}^-]}{[\text{AH}]} = -2$$

$$\rightarrow \frac{[\text{A}^-]}{[\text{AH}]} = 0.01 \text{ at pH} < \text{pK there is more AH}$$

$$\text{At pH 9} \quad -\log \frac{[\text{A}^-]}{[\text{AH}]} = (9.52 / 1.36 - 9) = -2; \rightarrow \log \frac{[\text{A}^-]}{[\text{AH}]} = 2$$

$$\rightarrow \frac{[\text{A}^-]}{[\text{AH}]} = 100. \text{ at pH} > \text{pK there is more A}^-$$

If a group has 2 choices (ionized and neutral) the system has 2 states.
 If there are n groups with 2 choices there is 2^n states.

With 1 acid the states are A^- and AH

If we set the energy of the AH state = 0 (arbitrary reference)

the energy of the A^- state is $pK - pH$ (this is the energy of the system when $[A^-]=[AH]$)

The concentration of a microstate at equilibrium =

$$\langle \text{state} \rangle = \langle \text{state}_i \rangle = \frac{10^{-\Delta G_i / kt}}{\sum_{i=1}^{\text{all states}} 10^{-\Delta G_i / kt}} \quad (\text{the sum is called the partition coefficient})$$

with these 2 states

AH \rightarrow $\langle 0 \rangle$ has a G defined as 0 so $10^{-\Delta G/kT} = 1$

$A^- \rightarrow \langle -1 \rangle$ has a G of $pK - pH$ (The energy for moving AH (G=0) to A^-)

if the $pK = 7$

at pH 5 $\langle 0 \rangle = 1/(1+10^{-pK-pH}) = 0.99$ $\langle -1 \rangle = 10^{-pK-pH}/(1+10^{-pK-pH}) = 0.01$

If there are 2 groups there are 2^2 states

the energy of

AH : AH is defined as 0

A_1^- : AH_2 is $pK_1 - pH + 0$ + interaction energy between A_1^- and AH_2

AH_1 : A_2^- is $0 + pK_2 - pH +$ interaction energy between A_2^- and AH_1

A_1^- : A_2^- is $pK_1 - pH + pK_2 - pH +$ interaction energy between A_1^- and A_2^-

The partition coefficient now has 4 terms.