4.10 Proton Competition and Keq

a) Question to Consider for any Acid and Base Equilibrium:

"Which side of the equilibrium is favored?"

(i.e.: which side, product or reactant, has a greater [ ])

(i.e.: if there are two acids in an equilibrium, which acid donates the proton better?)

$$CN^- + H_2CO_3 \rightleftharpoons HCN + HCO_3^-$$

b) Proton Competition (Method 1)

$$\underset{CB}{CN^-} + \underset{CA}{H_2CO_3} \rightleftharpoons \underset{CA}{HCN} + \underset{CB}{HCO_3^-}$$

i) The two acids are: H_2CO_3 and HCN

ii) The stronger acid will be a better proton donor:

H_2CO_3 Ka = 4.3×10^{-7} ← better H^+ donor!

HCN Ka = 4.9×10^{-10}

iii) Therefore, the forward reaction is favored because H_2CO_3 is more successful at making its products. Thus, the **product side of the equilibrium is favored**.

c) Keq (Method 2)

i) Keq for an acid-base equilibrium can have the form:

$$Keq = \frac{Ka(\text{reactant acid})}{Ka(\text{product acid})}$$

(if desired, see p.131 for how this formula is derived)

ii) $Keq = \frac{\text{Ka of } H_2CO_3}{\text{Ka of HCN}} = \frac{4.3 \times 10^{-7}}{4.9 \times 10^{-10}} = 880$

iii) Large Keq (Keq > 1) means the **product side is favored**.

d) Examples

i) When NO_2^- and $HC_2O_4^-$ are mixed:

a) What is the Bronsted-Lowry equilibrium?

$$NO_2^- + HC_2O_4^- \rightleftharpoons HNO_2 + C_2O_4^-$$

b) Does equilibrium favor products or reactants?

Method 1

Compare $HC_2O_4^-$ to HNO_2

HNO_2 is stronger, so reactants are favored.

Method 2

$$Keq = \frac{Ka(HC_2O_4^-)}{Ka(HNO_2)} = \frac{6.4 \times 10^{-5}}{4.6 \times 10^{-4}} = 0.14$$

Keq < 1 so reactants are favored.

ii) When HSO_3^- and $H_2PO_4^-$ are mixed:

a) What is the Bronsted-Lowry equilibrium?

$$HSO_3^- + H_2PO_4^- \rightleftharpoons SO_3^{-2} + H_3PO_4$$

(Note: it is not $HSO_3^- + H_2PO_4^- \rightleftharpoons H_2SO_3 + HPO_4^{-2}$ because between the two reactants, HSO_3^- is the stronger acid so HSO_3^- donates the proton)

b) Does equilibrium favor products or reactants?

Method 1

Compare HSO_3^- to H_3PO_4

H_3PO_4 is stronger, so reactants are favored.

Method 2

$$Keq = \frac{Ka(HSO_3^-)}{Ka(H_3PO_4)} = \frac{1.0 \times 10^{-7}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-5}$$

Keq < 1 so reactants are favored.

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