

On the Thermodynamic Feasibility of Acid-Base Equilibria

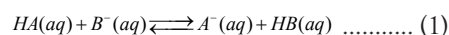
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DESCRIPTION

Most undergraduate Organic chemistry textbooks contain a section on the general acid-base equilibria, strength of acids and bases, and predicting the equilibrium position of acid-base reactions (1-3). The students are taught to qualitatively predict the directions of these reactions using only the acid/base strengths or acid/base constants (pK_a/pK_b) without elaborating how or why they work. For example, statements like ‘stronger acids/bases tend to move towards weaker forms’ are not good explanations (1-3). Moreover, finding an answer in analytical and physical chemistry textbooks specific to this question is challenging (4-6). The simple thermodynamic framework put forward here can easily explain why these predictions work and allow one to quantify the direction of acid-base reactions.

For a general acid-base reaction, consider an acid HA transferring a proton to the conjugated base B^- of an acid HB in an aqueous solution. The reaction forms the conjugated base (A^-) of the first acid, and HB.



The thermodynamic equilibrium constant (K_{eq}) for this reaction can be written as,

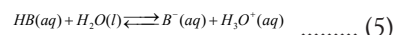
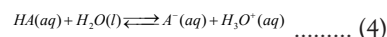
$$K_{eq} = \frac{[A^-(aq)][HB(aq)]}{[HA(aq)][B^-(aq)]} \dots\dots\dots (2)$$

According to equation (2), if the reaction moves forward, i.e., to convert most of the reactants into products, the equilibrium constant should be greater than unity ($K_{eq} > 1$). Furthermore, the second law of thermodynamics states that a chemical process that moves forward should produce a negative Gibbs free energy change ($\Delta G^0_{Overall}$) for the overall reaction (1-6) [1]. In addition, $\Delta G^0_{Overall}$ can be related to K_{eq} by the following equation,

$$\Delta G^0_{Overall} = -RT \ln K_{eq} \dots\dots\dots (3)$$

From equation (3), it is clear that a reaction with $K_{eq} > 1$ is also characterized by a negative ($\Delta G^0_{Overall}$) value. The next question is how to relate these thermodynamic quantities to pK_a/pK_b values of acids and bases. To do that, consider individual reactions of HA and HB with water, where they transfer a proton to a water

molecule acting as acids in an aqueous solution [2].



From these two reactions, we can define their acid constants (K_a) as follows,

$$K_{a,HA} = \frac{[A^-(aq)][H_3O^+(aq)]}{[HA(aq)]} \dots\dots\dots (6)$$

$$K_{a,HB} = \frac{[B^-(aq)][H_3O^+(aq)]}{[HB(aq)]} \dots\dots\dots (7)$$

As before, these thermodynamic equilibrium constants can be related to corresponding Gibbs free energy changes as follows,

$$\Delta G^0_{HA} = -RT \ln K_{a,HA} \dots\dots\dots (8)$$

$$\Delta G^0_{HB} = -RT \ln K_{a,HB} \dots\dots\dots (9)$$

Comparing the chemical equation (1) with (4) and (5), it can be shown that,

$$K_{eq} = \frac{K_{a,HA}}{K_{a,HB}} \dots\dots\dots (10)$$

Then the equation (3) can be written as,

$$\Delta G^0_{Overall} = -RT \ln \left(\frac{K_{a,HA}}{K_{a,HB}} \right) = -RT \ln K_{a,HA} + RT \ln K_{a,HB} \dots\dots\dots (11)$$

Converting the ln terms into a log terms and realizing $pK_a = -\log K_a$ produces,

$$\Delta G^0_{Overall} = -2.303RT \log K_{a,HA} + 2.303RT \log K_{a,HB} = 2.303RT (pK_{a,HA} - pK_{a,HB}) \dots\dots\dots (12)$$

The equation (12) can be directly used to calculate the feasibility and extent of a reaction using the acid/base constants of individual components [3]. For example, if $pK_a,HA < pK_a,HB$, then the value of $\Delta G^0_{Overall}$ will be negative, and hence HA will transfer a proton to the B^- to drive the reaction forward. The magnitude of $\Delta G^0_{Overall}$ determines the extent of the reaction. However, if $\Delta G^0_{Overall}$ is positive, the reaction is thermodynamically disfavored in the forward direction and favored in the reverse direction.

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Received: 06-Apr-2024, Manuscript No. JCEPT-24-30665; **Editor assigned:** 09-Apr-2024, PreQC No. JCEPT-24-30665 (PQ); **Reviewed:** 24-Apr-2024, QC No. JCEPT-24-30665; **Revised:** 01-May-2024, Manuscript No. JCEPT-24-30665 (R); **Published:** 08-May-2024, DOI:10.35248/2157-7048.24.15.497

Citation: Senavirathne G (2024) On the Thermodynamic Feasibility of Acid-Base Equilibria. J Chem Eng Process Technol. 15:497.

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In addition, if the pK_a of HA and pK_b of the B^- are given, one can modify the equation (12) as follows,

$$pK_{a,HB} + pK_{b,B^-} = 14 \quad \text{..... (13)}$$

Then,

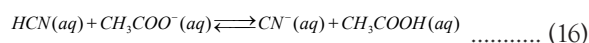
$$pK_{a,HB} = 14 - pK_{b,B^-} \quad \text{..... (14)}$$

Plugging the equation (14) into equation (12) yields,

$$\Delta G_{Overall}^0 = 2.303RT[(pK_{a,HA} + pK_{b,B^-}) - 14] \quad \text{..... (15)}$$

Equation (15) predicts that for the forward reaction to be thermodynamically feasible, the summation of the two pK_a of HA and the pK_b of the base B^- should be less than 14, or otherwise, the reverse reaction is more thermodynamically feasible [4].

Finally, we can demonstrate the applicability of the discussion in an actual example. If the pK_a of Hydrocyanic acid (HCN) is 9.22 and that of acetic acid (CH_3COOH) is 4.74, determine the favored determine for the following reaction [5].



Let's apply the equation (12) and calculate the $\Delta G_{Overall}^0$ for the above reaction assuming standard conditions ($T=298.15$ K and 1 atm pressure) and $R=8.314$ $Jmol^{-1}K^{-1}$

$$\Delta G_{Overall}^0 = 2.303 \times 8.314 Jmol^{-1}K^{-1} \times 298.15K(9.22 - 4.74) = 25.58 kJmol^{-1} \quad \text{..... (17)}$$

This calculation predicts that aqueous HCN will not transfer a proton to aqueous CH_3COO^- under standard conditions to

drive the reaction forward [6]. However, acetic acid would readily transfer a proton to aqueous cyanide to drive the reverse reaction in a highly exergonic fashion.

CONCLUSION

The simple thermodynamic framework explained here should allow the students to understand the basis for using K_a/pK_a values to predict the feasibility of acid-base reactions more logically and quantitatively and directly compare the robustness of different reactions. In addition, it may help them make connections between materials learned in Organic chemistry, such as the above example, and things they learn in analytical and physical chemistry on acid-base reactions, chemical equilibrium, and thermodynamics.

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