

Review Form 1.6

Journal Name:	Chemical Science International Journal
Manuscript Number:	Ms_CSIJ_89231
Title of the Manuscript:	Gibbs Free Energy change (ΔG) in Aqueous Dissociation of Benzoic Acid at Temperature 'K' : A Thermodynamic Study
Type of the Article	Review Article

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This journal's peer review policy states that **NO** manuscript should be rejected only on the basis of '**lack of Novelty**', provided the manuscript is scientifically robust and technically sound.

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PART 1: Review Comments

	Reviewer's comment	Author's comment (if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)
Compulsory REVISION comments	<p>The following questions aim to help the author to clarify some important aspects.</p> <p>CRc1) One of the main results shown in this work is: 1) in the Temperature range 289 K - 303 K, Ka is inversely proportional to temperature; 2) in the Temperature range 303 K - 314 K, Ka is proportional to temperature.</p> <p>In the manuscript, Ka denotes the “acid dissociation constant” (see the abstract and page 3 of the manuscript). However, we know that the above properties 1) and 2) are not satisfied by Ka, but by the “thermodynamic dissociation constant <i>pKa</i>”, defined as the negative logarithmic scale of Ka (i.e., <i>pKa</i> = -Log₁₀ Ka). The author is asked to clarify this point.</p> <p>CRc2) In this work, the author studied the solute benzoic acid (C₆H₅COOH). In a saturated aqueous solution, benzoic acid has a little molar solubility with the following equilibrium:</p> $C_6H_5COOH_{(aq)} \xrightleftharpoons{Kc} H^+_{(aq)} + C_6H_5COO^-_{(aq)} \quad (a)$ <p>In this case, we have to introduce 3 constants: Ka, Kc and I, defined as follows: i) Ka is the thermodynamic dissociation constant at infinite dilution at a given temperature; ii) Kc is the apparent thermodynamic dissociation constant at a given temperature; iii) I is the ionic strength. These three quantities are linked by the relations</p> $\log Ka + 2B\sqrt{I} = \log Kc \quad (b)$ <p>where B is a quantity that depends on some physical properties of the solution such as dielectric constant and temperature. However, on page 3 of the manuscript the author states: “Kc is called the dissociation constant (Ka)”. The author is asked to clarify his definition compared with relation (b) motivating its definition from the chemical point of view.</p> <p>CRc3) As mentioned in the above point CRc1), <i>pKa</i> shows two different behaviours in the range of Temperature 289 K - 303 K and 303 K - 314 K, respectively. However, a celebrated work of Smolyakov B. of 1996 (published in the review, <i>Russian Journal of Physical Chemistry</i>, 15(3):618-622 (1966) - not cited in this paper) established the values of the dissociation constants of benzoic acid in aqueous solutions at temperatures from 25 to 90 °C. More specifically, Smolyakov estimated the following temperature dependence of <i>pKa</i>, for the temperature interval from 0 to 150 °C:</p> $pKa = 804,7/T - 1,192 + 0,0090\ 476\ T \quad (c)$ <p>The author is asked to provide his/her comments about the following remarks: CRc3a) Eq. (c) shows that the term 804,7/T dominates for low Temperature whereas, for temperature sufficiently high, is the term +0,0090 476 T that dominates. This is in line with the findings reported in CRc1). CRc3b) The presence in Eq. (c) of the constant term (i.e., the term independent of T) allows the existence of a rather small “intermediate range of Temperature” where there is no regular correlation between <i>pKa</i> of benzoic acid and Temperature. The author - but before him Khouri S.J. in 2015 (see Re. [26]) - determined the relevant acid-point <i>pKa</i>=4.176 at T=25°C. Even in this case, Smolyakov's expression is in line with the results found by the author and by Khouri S.J.</p>	
Minor REVISION comments	<p>MRc1) This work is part of a series of manuscripts on the same subject previously appeared in literature. In particular, some results, herein reported, appear also in the paper published in 2015 in the review <i>American Journal of Analytical Chemistry</i> (Title: "Titrimetric Study of the Solubility and Dissociation of Benzoic Acid in Water: Effect of Ionic Strength and Temperature", Vol. 06, No.05, (2015), Article ID: 55356,7).</p> <p>MRc2) In short, we can say that this work shows four main results. However, these four findings have already appeared in international peer-reviewed scientific journals. (see the Section above: "Compulsory REVISION Comments").</p> <p>MRc3) Many mathematical expressions used in this work refer to expressions already appeared in other manuscripts and used to deal with the exact same problem. However, citations are sometimes chronologically incorrect. For</p>	

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	<p>instance, consider Eq. (4). In this case the author cites the Ref. [26], which dated 2019 (Lima EC, H-Bandegharai A, M-Piraján JC, Anastopoulos I. Journal of Molecular Liquids. 273: 425-434 (2019)) when, in reality, this equation had already been used in 2015 by Khouri S.J. (see Eq. (10 in Ref. [18], Khouri S.J., American J. Analytical Chem. 6: 429-436 (2015)).</p> <p>MRc4) Please, check the English of the article; several typos have been detected.</p> <p>MRc5) Some nomenclatures used in the manuscript need clarification (see the Secion above).</p>	
Optional/General comments	<p>This work is vulnerable in several respects:</p> <p>1) the suggestions expressed in Section CRc) show that, at first glance, the main results reported in this manuscript were already known and have already appeared in the literature. To avoid unpleasant objections from the reader, it is essential that the author shows the added value of his results.</p> <p>2) there are several inaccuracies (<i>pKa</i> instead of <i>Ka</i>) or definitions (<i>Kc</i>, <i>Ka</i>) that must be clarified.</p> <p>3) Besides, the presence of many typos requires a thorough revision of the English text.</p>	

PART 2:

	Reviewer's comment	Author's comment (if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)
Are there ethical issues in this manuscript?	(If yes, Kindly please write down the ethical issues here in details)	

Reviewer Details:

Name:	Giorgio Sonnino
Department, University & Country	Universite' Libre de Bruxelles (ULB), Belgium