

Investigating the Thermodynamic Causes Behind the Anomalous Large Shifts in pK_a Values of Benzoic Acid-Modified Graphite and Glassy Carbon Surfaces [*Langmuir* 2007, 23, 7847]. Poobalasingam Abiman, Allison Crossley, Gregory G. Wildgoose, John H. Jones, and Richard G. Compton*

Figure 4a,b and the values in Tables 1–3 were incorrect as published. The corrected figures, values in tables and conclusion should be as follows:

In conclusion, enthalpic contribution was neglected by mistake, but it cannot be neglected, and the different surface pK_a values were found to be controlled by both the enthalpic and entropic terms. The ΔH° values for BAcarbon powder and BA-GC are different in sign; both ΔS° values are appreciably different from the values in bulk solution (Tables 1–3). The lateral interactions on the carbon surface and/or hydrogen bond formation are responsible for the enthalpic contribution, whereas the entropic contribution attributed to the ordering of solvent molecules at the interface between the carbon substrate and the solution is likely responsible for the variation in the observed pK_a values, reflecting the different hydrophobicity/hydrophilicity of the graphite and glassy carbon surfaces.

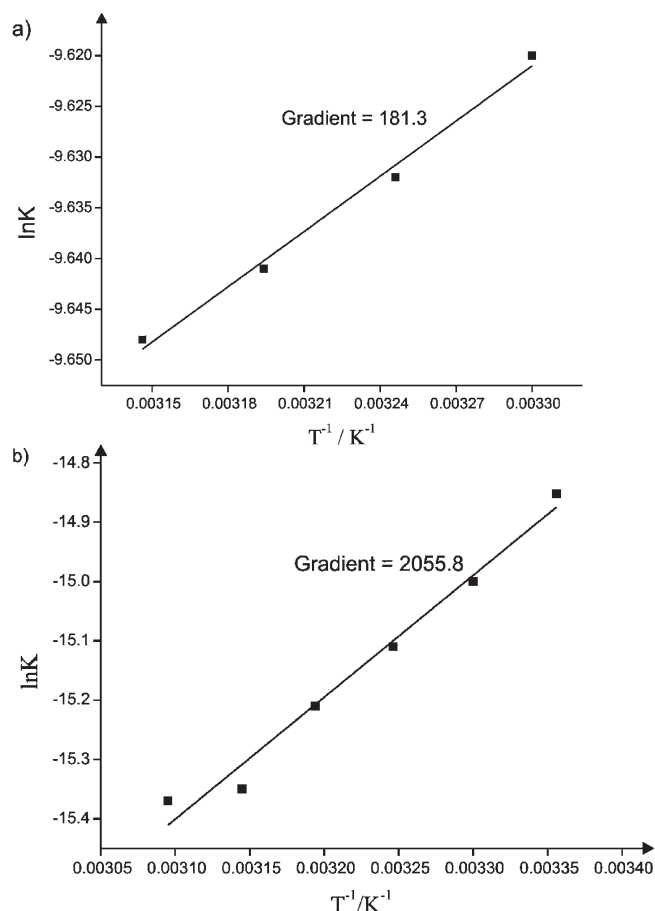


Figure 4. Plots of $\ln K_a$ versus $1/T$ for (a) benzoic acid in solution and (b) BAcarbon.

Table 1. Tabulated Values of the Change in Gibbs Energy and Entropy for the Ionization of Benzoic Acid in Solution from 25 to 45 °C^a

$T/^\circ\text{C}$	ΔG° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
25	23.8	-84.9
30	24.2	-84.8
35	24.7	-85.0
40	25.0	-84.7
45	25.5	-84.9
25 (literature value, ref 20)	24.0	-81.0

^a $\Delta H^\circ = -1.5$ kJ mol⁻¹.

Table 2. Tabulated Values of the Change in Gibbs Energy and Entropy for the Ionization of BAcarbon Powder from 25 to 50 °C^a

$T/^\circ\text{C}$	ΔG° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
25	36.8	-180.5
30	37.8	-180.9
35	38.7	-180.8
40	39.6	-180.8
45	40.6	-181.1
50	41.3	-180.4

^a $\Delta H^\circ = -17.0$ kJ mol⁻¹.

Table 3. The tabulated values of the change in Gibbs energy and entropy for the ionization of BA-GC powder from 25 to 50 °C. $\Delta H^\circ = 12.7$ kJ mol⁻¹

$T/^\circ\text{C}$	ΔG° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
25	18.5	-19.3
30	18.5	-18.9
35	18.6	-19.0
40	18.7	-19.0
45	18.8	-19.1
50	19.0	-19.3