Comment by Dr Ricardo Fritzsche

A paragraph in page 5 (Bamforth 2023) reads ‘The relative balance of carbonic acid and bicarbonate is dependent on pH. The pKa for this equilibrium is 3.6 at 25°C. Accordingly, at the pH range of most beers, the preponderance of the carbonic acid is in the form of bicarbonate.’

The pKa of carbonic acid in water at 25°C is 6.35-6.37 depending on the source; the pKa in beer could be slightly different but not 500-fold different. One could argue that it was just an editing error (i.e., 6.3 instead of 3.6), but the statement that ‘in most beers, the preponderance of the carbonic acid is in the form of bicarbonate’ indicates that Professor Bamforth meant to write that the pKa of carbonic acid is 3.6, which is incorrect. It can be experimentally demonstrated that there’s no significant bicarbonate in most beers (pH 4.5 and lower).

As we all know, pKa and pH are equal when half of the acid has dissociated. If the pKa of carbonic acid were 3.5, then beers at a pH of 4.1-4.3 will be full of bicarbonate. More than half of the CO₂ in beer would convert to bicarbonate. I have seen over 100 beers analyzed for bicarbonate and the value has almost always been zero (or very small if pH was 4.3-4.4).

I agree that there’s some odd chemistry that may render the pKa concept not applicable to carbonic acid/bicarbonate, but the key scientific question applicable to beer is whether for brewing purposes, the half point of the carbonic acid/bicarbonate equilibrium is 3.5 or much, much higher.
Response by Professor Charles Bamforth

It has been suggested that the value I quote (3.6) for the pKa of carbonic acid in my paper is incorrect. It is however based on the values for the true pKa of this acid cited in detailed investigations (Loerting and Bernard 2010; Pines et al. 2016) where the differentiation is drawn between this and the ‘apparent’ pKa of around 6.35 which involves the equilibrium constant for aqueous CO\textsubscript{2} in equilibrium with H\textsubscript{2}CO\textsubscript{3}.

I should also clarify another matter in relation to this. I point out in my paper that, in view of this pKa value, most of the carbonic acid present will be in the form of bicarbonate. The reader will appreciate however, that the vast majority of the carbon dioxide present in beer is in the form of CO\textsubscript{2} (c.f. the equilibrium constant cited in the paper). Even for the most highly carbonated beers, the levels of bicarbonate would be expected to be very low. Those seeking to quantify the level of bicarbonate in beer should ensure that the method employed cannot involve the prior decarbonation of the liquid.

References

