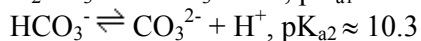
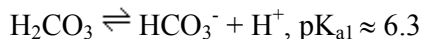
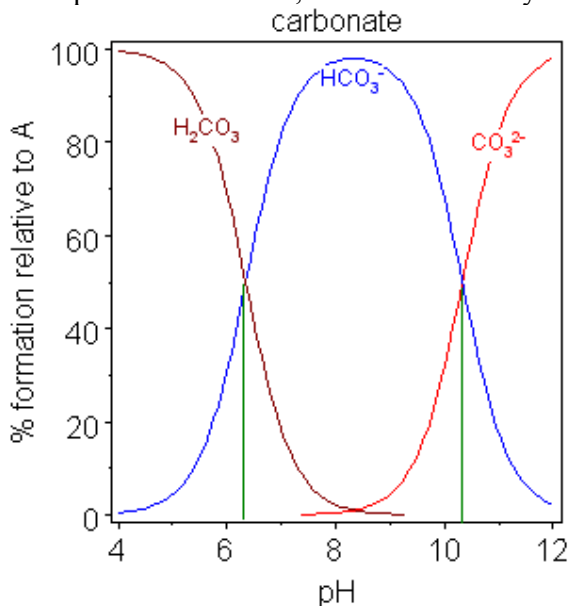


## Carbonate impurity, its effect on titration curves.

Carbonate is easily formed when atmospheric carbon dioxide is absorbed by an alkaline solution. If one assumes that once the  $\text{CO}_2$  has been absorbed it remains in solution, there are two equilibria to consider.

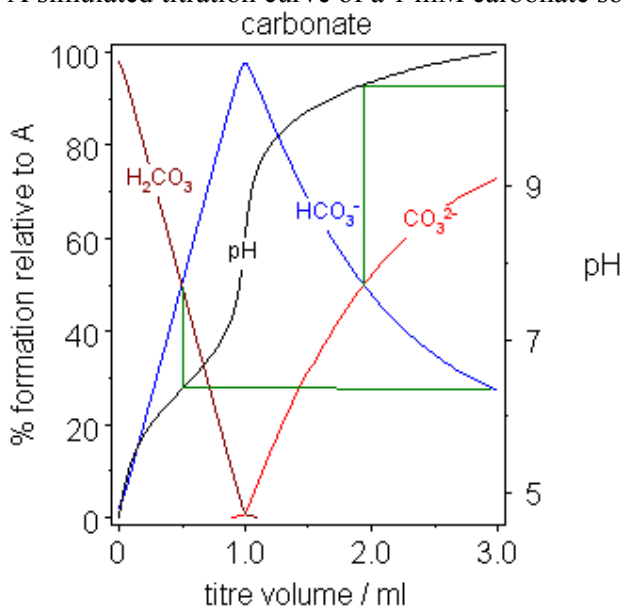


The species distribution, calculated with HySS, is as follows.



The vertical green lines are drawn at  $\text{pH} = \text{pK}_{\text{a}}$ , where the concentrations of the two species in equilibrium with each other are equal. These are the pH values at which the buffer capacity (see [http://en.wikipedia.org/wiki/Buffer\\_solution](http://en.wikipedia.org/wiki/Buffer_solution) for details) of the solution is a maximum.

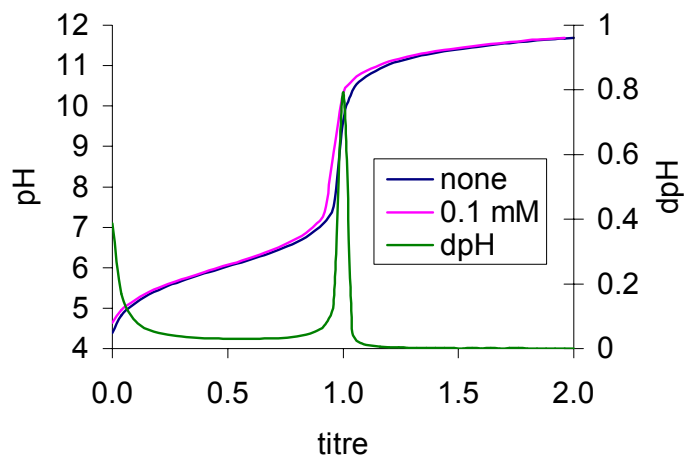
A simulated titration curve of a 1 mM carbonate solution with 0.01M alkali is shown next



This shows that there are two buffer regions where the pH rises relatively slowly, centred on the  $\text{pK}_{\text{a}}$  values, and extending roughly 1 pH unit on either side.

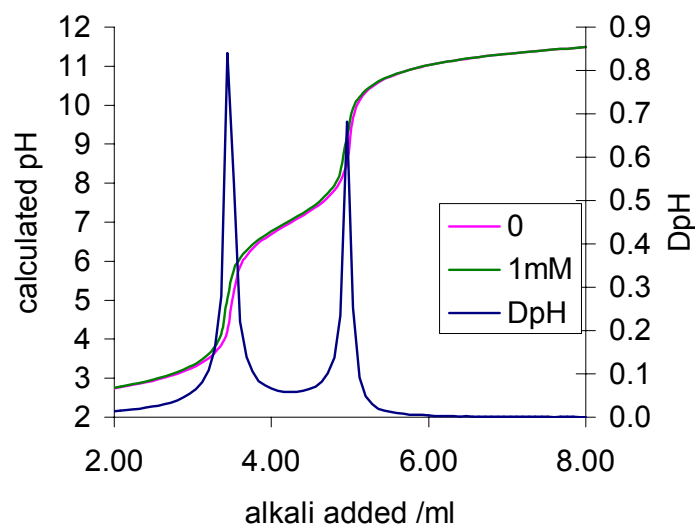
## Effect of carbonate impurity on titration curves.

The following plot is based on simulated titrations of a weak acid ( $pK = 6$ ) solution with 0.1M alkali containing either no carbonate or a 0.1mM carbonate concentration, that is, a 0.1% carbonate contaminant. The difference between pH values (with carbonate – without carbonate) for the two titration curves rises to a maximum at the equivalence point.

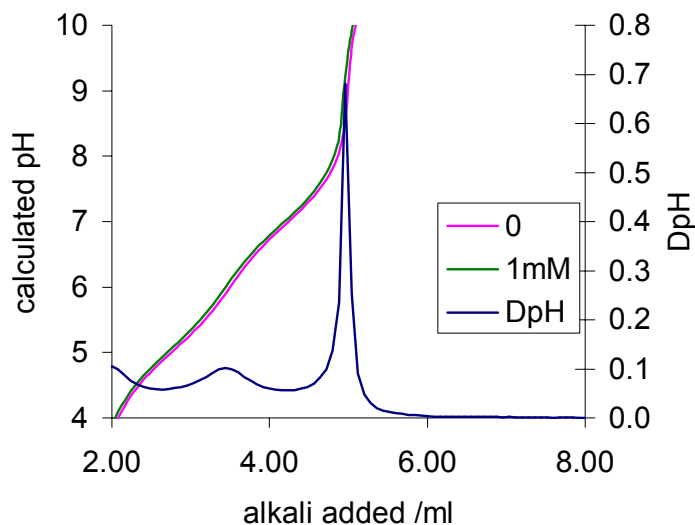


In this case the effect of carbonate on the pH in the region  $pH = pK \pm 1$  is minimal, so the determination of the stability constant value will not be affected.

Next, a titration of a dibasic acid with  $pK$  values of 2.5 and 7



When the two  $pK$  values are close together ( $pK_1=5$ ,  $pK_2=7$ ) the first end-point all but disappears.

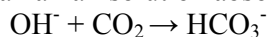


## Silicate impurity

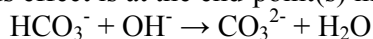
If the alkali is stored in a glass vessel, silicates will be slowly dissolved. As silicates are weak acids, they will have an effect on experimental titration curves.

## Conclusions

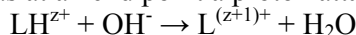
When an alkali solution absorbs  $\text{CO}_2$  the concentration changes,



The concentration change may be almost imperceptible. If alkali is contaminated with carbonate the most obvious effect is at the end-point(s) in a titration curve. This is because some alkali is consumed in the reaction



whereas at an end point a proton attached to a ligand is being neutralized.



The general effect of carbonate contamination is that, for a given titre, the pH is higher than it should be. When a stability constant is determined from such a titration curve, the carbonate impurity will introduce an error in the refined stability constant value.

Note. The effect of carbonate contamination is different from the effect of an error in total mmoles H. In the latter case a small adjustment of the value will bring the observed and calculated end-points into coincidence with each other, but this does not happen with carbonate contamination.

Alkaline solutions should be protected against absorption of atmospheric carbon dioxide at all times, before, during and after a titration. The burette and titration cell can be protected by soda-lime guard tubes, but a better procedure is to have a sealable system kept under a small positive pressure of an inert gas such as nitrogen or argon. The gas should be pre-saturated with water so as not to cause evaporation of the analyte solution.