

VARIATION OF SPECIFIC ROTATION WITH TEMPERATURE

Specific Optical Rotation of many materials depends on temperature and there are many references to the existence and importance of this effect. The studies published are mostly on materials of large commercial interest like sucrose and other sugars.

With the few published studies on other materials, the values reported have to be interpreted with caution owing to the presence of partially cancelling various parameters involved. Some of these are illustrated here.

Temperature at which the solvent is made up to volume, a solution made up at one temperature and measured at another temperature would have an implicit error owing to thermal expansion of the solvent. Water, a typical solvent, expands in volume by about 0.1% for a 5°C rise in temperature affecting the concentration by that factor. Left uncorrected for, this effect depresses the calculated values by 0.1%.

Temperature of the flask when made up to volume, a typical 100 ml glass volumetric flask changes by about 0.1 ml (0.1%) for a 5°C change in temperature. This leads to under estimation of specific rotation measured at higher temperatures.

Temperature of sample cell, a change in the length of the sample cell due to thermal expansion of the material of the cell (glass or stainless steel normally) has to be considered for accurate investigations. Length of a 200 mm glass cell would increase by 0.01 mm with a change of temperature from 20 to 25°C. Stainless steel cells change by 0.06 mm (0.03%) leading to over estimation at higher temperatures.

Changes in the scale of the Polarimeter with temperature, this is not pertinent in the modern Polarimeters which use rotary polarizer's.

The magnitude of all of these various parameters is small, but is still of the order of the expected variation due to the sample itself. They are not all of the same sign and cancel each other partially. The temperature co-efficient of sucrose for example is of the order of + 0.02% and is smaller than some of the effects considered above.

Without a thorough identification the reported values of specific rotation at various temperatures may not be usable or reproducible in a measurement made under different set of conditions. Accordingly temperature variation of specific rotation is seldom considered or corrected for explicitly.

The most accurate measurements are performed strictly at the specified temperature taking care to maintain all the glass ware, sample cells, solvents, material under investigation and the solvent at that temperature within specified limits. USP specifies for example that the temperature be $25 \pm 0.2^\circ\text{C}$, whereas the sugar trade bases the payments for sugar on the values measured at $20 \pm 0.2^\circ\text{C}$.