Letters to the Editors

The Pressure Correction in GC

Dear Editor:

I agree with the two discussions reported in this journal [1, 2] concerning the pressure or compressibility correction in GC, but I think some of the deductions need to be discussed further in order to obtain a better understanding. Unless otherwise stated, the symbols used here are the same as those used in references [1] and [2].

GC processes can be divided into two parts: dynamic and thermodynamic, both of which relate to GC conditions, but in different ways. It is commonly accepted that the former depends on the column temperature T and pressure P , while the later depends only on T . Under given conditions, it is the thermodynamic differences that make a mixture being separated by time and space into a dynamic process. Thus as a means of separation, the main purpose of GC is to obtain a retention value that closely relates to thermodynamics, and hopefully is independent of GC conditions.

As mentioned above, the thermodynamic process is independent of pressure; then, what does it mean to make a pressure correction to the retention volume? If the V_R^0 represents an amount of ideal gas, say the carrier gas, then it closely relates to T and P . There are many ways to describe the well-known and classical pressure correction factor j [3]

$$j = \frac{3}{2} \cdot \frac{\left(\frac{p_i}{p_0}\right)^2 - 1}{\left(\frac{p_i}{p_0}\right)^3 - 1} = \frac{3}{2} \cdot \frac{\left(\frac{u_0}{u_i}\right)^2 - 1}{\left(\frac{u_0}{u_i}\right)^3 - 1}$$
$$= \frac{p_0}{p_{ef}} = \frac{p_0}{\bar{p}} = \frac{\bar{u}}{u_0} = \frac{V_M^0}{V_M} = \frac{V_R^0}{V_R}$$

Here p_{ef} is the same as the $\bar{p}$ in [2], but in this reference the $p_0 = \bar{p} \cdot j$ was typed in error as $p_0 = \bar{p}/j$ several times. Then we have

$$V_R^0 \cdot p_{ef} = V_R \cdot p_0$$

In fact, correction of V_R with j just involve gas state transform from one state of (T, p_0, V_R) to another state of (T, p_{ef}, V_R^0) , therefore, the obtained V_R^0 also closely relates to a p_{ef} for a given T , and if V_R^0 is used as a thermodynamic value, it seems to be in conflict with the commonly accepted experimental fact. This is just what Davankov was concerned about.

Is V_R^0 really dependent on GC pressure condition then? Let us consider V_R^0 in a different way:

$$V_R^0 = V_R \cdot j = V_M \cdot j \cdot (1 + k') = V_M^0 \cdot (1 + k)$$

It is generally known that k is a pure thermodynamic dimensionless parameter, and V_M^0 is the geometrical volume of the column. It is important to bear in mind that, physically, geometrical volume is intrinsically different from gas volume. Then it follows that V_R^0 can serve as a thermodynamic parameter taking absolute geometrical volume as the reference standard. Actually the reason for the deviation cited in [1] had been addressed experimentally in the original paper [4]. Up to now, no sound evidence of obvious pressure effects on thermodynamic parameters has been reported in the literature, and no experiment had ever been designed purposely to testify the effect. The method proposed by Ettre et al. [5] may be used for this purpose. In commonly used GC conditions, no obvious non-ideal gas effect, such as in SFC mentioned in [2], has ever been reported.

To my understanding, Prof. Davankov is concerned more about thermodynamics as in his statement that "all retention values which incorporate the correction factor j relate to the effective pressure in the column ...since the corrected volumes are employed in thermodynamic estimations", while Prof. Blumberg is concerned more about dynamics as rephrased that "all retention values which incorporate the correction factor j relate to the average velocity of carrier gas in the column". Thermodynamically or dynamically, pressure correction bases on the same fact that pressure does not distribute uniformly along the GC column.

Since there may be some ambiguity to users, I would like to note here that the aim of the j correction is to make V_R^0 independent of pressure conditions in GC. V_R is hardly to be reproduced in different laboratories while V_R^0 is easy for a given column. The importance of pressure correction is self-evident here, and its importance may be added in the IUPAC document referring to j . I very much appreciate reading other proposals on this issue.

References

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Zhiyong Wu

Center of Chemistry and Physics Analysis, Hebei University, Baoding, 071002, P.R. China