Letters to the Editors

paring this result with the r.h.s. of Eq. (16), one comes to conclusion that, for a **uniform** k , $j_R = j_M$.

Similarly to the requirement for the uniformity of the viscosity-dependent γ in the previous section, the requirement for the uniform k in this derivation can have several physical interpretations. The most practically relevant set of conditions providing for the uniform k can be expressed as conditions C3c, C5 and C6 (main text).

Comment on the Letter of Zhiyong Wu

Zhiyong Wu is absolutely correct in his principal statement, namely, that by multiplying the experimentally measured retention volume, V_R , with the correction factor j we convert the carrier gas from one state (V_R, p_0, T) to another state ($V_R^0, \bar{p}, T$), i.e., to the real state of the mobile phase in the column, where $\bar{p}$ is the average pressure in the column. This is the only way to arrive at the thermodynamically valid value of retention volume, which then logically relates to the geometrical volume of void space in the column, V_M^0 , and the retention factor, k , of the solute as $V_R^0 = V_M^0(1 + k)$. This conversion fully reflects the physical sense of the correction factor, $j = p_0/\bar{p}$.

On the other hand, I am not happy about distinguishing two parts, dynamic and thermodynamic, in the GC process, as Wu suggests. If the mass transfer is fast and the phase distribution of the solute does not differ from the equilibrium value, then we are dealing with equilibrium chromatography and consider thermodynamically based phenomena, only. (Non-equilibrium chromatography, with flow rates too fast and mass transport too slow, would be a totally different, *kinetic* story). Therefore, as a thermodynamically sound retention

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value, V_R^0 does not depend on pressure, *provided that the system behaves ideally*. The latter condition implies that both the gas phase and the (stationary) liquid phase behave as ideal mixtures and the carrier gas does not compete or interact with the adsorbate in one way or another. Any deviation of the gas and/or liquid phase from ideal behavior would cause a dependence of the corrected retention volume, V_R^0 , on the pressure in the column. These deviations have recently attracted some attention, and a special term, "barochromatography", has been coined for fine tuning the selectivity of separations due to the non-ideal behavior of the system at elevated column pressures [1 and references therein].

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