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Vacuum thermochromatography - theory and Monte Carlo simulation

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Vacuum Thermochromatography –Theory and Monte Carlo Simulation
Mixtures of ultra low amounts of species can be separated in a tube, evacuated well below a microbar, along which the temperature gradually decreases from the closed hot end, by placing the sample into this hot end (zero coordinate). Then the Knudsen flow results in that the components with dissimilar adsorbability on the tube surface make deposits, which peak in different temperature intervals away from zero. It happens despite the absence of any convective flow, which is the basis of all true "chromatographies". A few experimental works published to date demonstrate separations of both very volatile and quite nonvolatile species.
This "vacuum thermochromatography"(VCT) is based on erratic independent displacements of the molecules up and down the tube. Indeed, a molecule experiences free flights between two sequential collisions with the tube wall, while each strike results in an adsorption event and so in an adsorption sojourn time. Thus the molecule does not keep memory about its incoming velocity vector; it is commonly supposed that the angular distribution of the rebounds follows the cosine law.
The paper presents the first rigorous consideration of the microscopic picture of VCT to substantiate MC simulations. Formulae for the flight length and its projection on the tube axis were derived. Algorithms of calculating random values and the probability density functions for the above quantities were obtained. Erroneous formulae and values met in literature were corrected.
In an isothermal tube, the picture obtained by MC simulations was indistinguishable from the solution of the corresponding diffusion problem. It is the half-Gaussian –because the migration is reflected at zero – and the mixture components differ only in the width of that distribution. However, in the case of VTC, the average adsorption sojourn time, which is proportional to the Boltzmann factor (depending exponentially on the desorption energy), rapidly increases with lower temperature. As a result, two molecules displaced from the given coordinate in opposite directions have different probability per unit time to make next steps. This is the background for evolution of the adsorption peak, which "moves"towards lower temperature with longer duration of the experiment.
Empirical regularities in the peak coordinate and temperature of the simulated peaks as a function of some experimental conditions were obtained. Some reasonable function for fitting the peak profiles was proposed. Attempts to use the diffusion ansatz for the interpretation of VCT data were undertaken though the strong temperature change of the effective diffusion coefficient with the coordinate brings problems in diffusional description.
VCT as a method of preparative separation offers prospects of solving some specific task in radiochemical analyses. One of the goals is finding the energy of desorption of various species . The here obtained equations with semi-empirical parameters allow thermodynamic interpretation of the experimental data. The earlier attempts on these lines are critically discussed.
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