The retention index is a measure of the standard chemical potential of a volatile substance in an ideal dilute solution compared to the ideal gas state. The solvent is the stationary phase in gas chromatography. Retention indices can be calculated from the structure of the solute, and they can be used to measure interaction forces between molecules. [The SCP indicates that this paper has been cited in over 255 publications, making it the most-cited paper from this journal.]

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February 16, 1988

In gas chromatography, the logarithm of the net retention volume of the members of the homologous series of the n-alkanes, \( C_{n}H_{2n+2} \), gives a nearly linear plot as a function of carbon number \( n \). By designating the logarithmic retention of the \( n \)-alkanes as \( R_{f} \), the position of a peak can easily be characterized by linear interpolation between two adjacent \( n \)-paraffins eluted before and after the compound. It is very easy to show that the resulting "retention index" is a measure of the standard chemical potential difference of the compound in question. The fixed points are the standard chemical potential differences of the \( n \)-alkanes that are nearly equidistant with the carbon number. This function compares the chemical potential of a substance in an ideal dilute solution with that in the ideal gas state.

In the gaseous state, the molecules of the solute are not attracted by the force field of neighboring molecules. In the ideal dilute solution, they are in intimate contact with the stationary phase, the solvent. In such an equilibrium system, the force of intermolecular attraction is relatively weak, and, in first approximation, the entropy introduced by this force is proportional to it. In other words, the molar entropy difference is proportional to the molar enthalpy.

The first consequence of this proportionality is that the retention index is practically independent of temperature. The second consequence is that one can treat retention indices as if they are a measure of interaction forces between the solute and the force field of the solvent molecules. In a first approximation, dispersion forces and polar forces are additive. Therefore, retention indices can be predicted by additivity rules on the basis of the structure of the solute. Rules could be also be given for the calculation of the additional retention of a compound, \( \Delta R \), on a polar stationary phase compared to the retention on a nonpolar solvent. Let me mention some early applications. L. Rohrschneider has shown that, with the help of five \( \Delta R \)-values of judiciously chosen molecular probes, the polarity of a solvent could be characterized and that with the help of this "property vector," retention could be predicted.1 B.L. Karger, L.R. Snyder, and C. Eon deduced a set of "solubility parameters" by extending the concept of J.H. Hildebrand and R.L. Scott.2 Also, the \( \Delta R \)-values were seen to correlate with olfactory quality of substances.3 Obviously, \( \Delta R \)-values characterize the polarity of a solute and of a solvent in some detail. They can be related to other polarity scales.4

This paper was written on invitation and was presented at the 4th International Chromatography Symposium held in Houston, Texas (chairman: Albert Zlatkis). In the introduction, the state of the art was summarized with a critical evaluation of experiments described in the literature. The predictive power of the retention index system was then presented in the form of rules. They were formulated for the prediction of chromatographic data, but it was obvious that they are also valid for the prediction of Henry coefficients in ideal dilute solutions of nonionic species.

It was planned that the lectures presented would be published in Analytical Chemistry. My paper, however, was promptly refused for publication by a referee whose name I have forgotten. After a long discussion in the hotel room, the symposium headquarters, I left the room in the mood to throw away my manuscript. In the corridor, I met Roy Keller to whom I exclaimed my misadventure. After I finished, Roy responded: "I will buy the manuscript." This is how it became published in the Advances in Chromatography series.