Title: **Enthalpy-entropy compensation effect: verification of a chemical model by numerical simulations**

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Many homologous reaction series present linear correlations between the enthalpy ($\Delta H^{\circ}_{\neq,\mathrm{i}}$) and entropy ($\Delta S^{\circ}_{\neq,\mathrm{i}}$) of activation (kinetic compensation effect), the slope being the isokinetic temperature of the series (T_{iso}), so that at $T = T_{\mathrm{iso}}$ all the reactions of the family share the same value of the rate constant. Unfortunately, however, the random errors committed in the laboratory in the determination of $\Delta H^{\circ}_{\neq,\mathrm{i}}$ and $\Delta S^{\circ}_{\neq,\mathrm{i}}$ are interrelated, and so tend to produce false isokinetic relationships. As a result, the existence of physically meaningful isokinetic relationships is a topic of lasting controversy. In this research project, it is shown that both the LFER-type (either Hammett or Taft) and isokinetic linear correlations are direct consequences of two more basic correlations, those of $\Delta H^{\circ}_{\neq,\mathrm{i}}$ vs. σ_{i} and $\Delta S^{\circ}_{\neq,\mathrm{i}}$ vs. σ_{i} , where the abscissa is the Hammett (or Taft) substituent parameter. A mathematical model has been developed, according to which T_{iso} can be interpreted as the temperature at which the reaction constant obtained as the slope of the LFER-type straight line takes a zero value ($\rho = 0$). Moreover, the numerical simulations performed indicated that the $\log k_{\mathrm{T}}$ vs. σ_{i} and $\Delta H^{\circ}_{\neq,\mathrm{i}}$ vs. $\Delta S^{\circ}_{\neq,\mathrm{i}}$ linear plots can be visualized as two faces of the same coin, since, if the kinetic data obey the first law with a high correlation coefficient, the probability of fulfillment of the second will be very high. Finally, it has been found that values of T_{iso} and T_{δ} (the slope of the linear correlation between the enthalpy-entropy deviations) very close to the mean working temperature, as well as correlation coefficients of the $\Delta H^{\circ}_{\neq,\mathrm{i}}$ vs. $\Delta S^{\circ}_{\neq,\mathrm{i}}$ linear plots much higher than those corresponding to the $\Delta H^{\circ}_{\neq,\mathrm{i}}$ vs. σ_{i} and $\Delta S^{\circ}_{\neq,\mathrm{i}}$ vs. σ_{i} plots, are all indicative of false isokinetic relationships, highly contaminated by the statistical correlation between the enthalpy and entropy experimental errors.