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Time distribution of adsorption entropy of gases on heterogeneous surfaces by reversed-flow gas chromatography

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Abstract

The reversed-flow gas chromatography (RF-GC) technique has been applied to measure the adsorption entropy over time, when gaseous pentane is adsorbed on the surface of two solids (γ-alumina and a silica supported rhodium catalyst) at 393.15 and 413.15 K, respectively. Utilizing experimental chromatographic data, this novel methodology also permits the simultaneous measurement of the local adsorption energy, ε, local equilibrium adsorbed concentration, c_s^*, and local adsorption isotherm, $\theta(p, T, \varepsilon)$ in a time resolved way. In contrast with other inverse gas chromatographic methods, which determine the standard entropy at zero surface coverage, the present method operates over a wide range of surface coverage taking into account not only the adsorbate–adsorbent interaction, but also the adsorbate–adsorbate interaction. One of the most interesting observations of the present work is the fact that the interaction of *n*-pentane is spontaneous on the Rh/SiO_2 catalyst for a very short time interval compared to that on γ-Al_2O_3. This can explain the different kinetic behavior of each particular gas–solid system, and it can be attributed to the fact that large amounts of *n*-C_5H_{12} are present on the active sites of the Rh/SiO_2 catalyst compared to those on γ-Al_2O_3, as the local equilibrium adsorbed concentration values, c_s^*, indicate.

Keywords: Adsorption entropy; Time-resolved chromatography; Reversed-flow gas chromatography

1. Introduction

It seems that old inverse gas chromatography cannot distinguish between various adsorption sites, as regarding adsorption energy and entropy. In contrast to that, time-resolved inverse gas chromatography can make some noticeable distinctions of adsorption energy distribution functions against adsorption energy, and against time of measurement. It is thus interesting to measure adsorption entropies. As to its methodology, the reversed-flow gas chromatography (RF-GC) technique can be employed as described in three recent reviews [1–3] and a recent book [4].

Chromatographic separation is based on physicochemical processes such as diffusion and adsorption. Diffusion, adsorption and possible surface reaction(s) are also closely interconnected in heterogeneous catalysis. Furthermore, the nature of the active sites is one of the pervasive problems in heterogeneous catalysis as well as in chromatography, since every adsorbent includes various active sites, characterized by different adsorption strength and adsorbate mobility. The changes of the standard entropy, ΔS, enthalpy, ΔH, as well as of Gibbs free energy, ΔG°, are fundamental factors governing physical and chemical processes. In this work, the methodology for the measurement of thermodynamic parameters related to gas–solid interactions is reviewed. This methodology permits the simultaneous measurement of the local adsorption energy, ε, the local equilibrium adsorbed concentration c_s^*, and the local adsorption isotherm $\theta(p, T, \varepsilon)$, from which the local thermodynamic parameters ΔS, ΔG° and ΔH are determined, as described later in Section 2. The term “local” means that it refers to a certain time t, i.e., involving not all adsorption energy sites, but only those active at time t.

The majority of inverse gas chromatographic (IGC) measurements require infinite dilution and fast equilibration of the injected solute between the stationary and mobile phase. These demands are also achieved by using RF-GC methodologies.

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However, the usual inverse gas chromatography, in which the stationary phase is the main object of investigation, is a classical elution method, which neglects the mass transfer phenomena and does not take into account the sorption effect. In contrast to that integration method, the novel methodology of RF-GC, although being an inverse gas chromatographic technique, is a differential method, not depending either on retention times and net retention volumes, V_N, or on broadening factors and statistical moments of the elution bands. The results of the new methodology of RF-GC are based on a non-linear adsorption isotherm model, over an extended period of time. Thus, RF-GC is a time-resolved chromatography, exhibiting different behavior with sampling time. Its "sample peaks" constitute a sampling procedure for various physicochemical quantities, as described in detail in the recent book [4].

The adsorption of *n*-pentane (n-C_5H_{12}) over two different solids was selected as a model system for an evaluation of the methodology. The two different solids, i.e., a conventional adsorbent (γ-Al_2O_3) and a three-way catalyst containing 3% (w/w) Rh supported on SiO_2, are expected to affect the behavior of each particular gas–solid system in a different way. This is the main reason for a first generalization of the system behavior.

2. Theoretical

Boudart et al. [5] suggested empirical guidelines to determine whether it would be inconsistent for the kinetically obtained K_{exp} to be an adsorption equilibrium constant. The guidelines involve the entropy of adsorption ΔS_{ads} obtained by the variation with temperature of K_{exp} as:

$$\ln K_{\text{exp}} = \frac{\Delta S_{\text{exp}}}{R} - \frac{\Delta H_{\text{exp}}}{RT} \qquad (1)$$

In 1978, Katsanos et al. [6] in the frame of thermodynamics of adsorption based on gas –solid chromatography, have determined experimentally both the differential enthalpy ΔH_{ads} and the differential entropy of adsorption ΔS_{ads} based on the equation:

$$\ln V_N = \ln(RTn_s) + \frac{\Delta S_{\text{ads}}}{R} - \frac{\Delta H_{\text{ads}}}{R}\frac{1}{T} \qquad (2)$$

where n_s is the total amount of the substance in the adsorbed state. The method was based on the variation of the net retention volume V_N with temperature.

Later, Knox and Dadyburjor [7] developed the bounds for acceptable values of adsorption entropy. In 1993, Lopez-Garzon et al. [8] used simple inverse gas chromatography to calculate standard free energy, enthalpy and entropy of adsorption of *n*-alkanes using the same Eq. (1) in the form $\Delta S = (\Delta H - \Delta G)/T$. Keeping in mind that $\Delta G = -RT \ln K_{\text{exp}}$, one finds Eq. (1) by substituting in the above $\Delta G/T = -R \ln K_{\text{exp}}$.

More recently Bakaev and co-workers [9–12] used inverse gas chromatography to study the entropy distribution of adsorption sites on heterogeneous glass fiber surface. The classical Eq. (1) has been derived again [12] in the form:

$$K'_{\text{H}} = \exp\left(\frac{\Delta S_i}{R}\right) \exp\left(-\frac{\Delta U_i}{RT}\right) \qquad (3)$$

where K'_H is the Henry constant, and ΔU_i and ΔS_i are the changes of the energy and the entropy, respectively, for a mol of molecules adsorbed on *i*-sites and the same molecules in the ideal gas state.

Since $V_N = W_s K_p$, where W_s is the total mass of the stationary phase in gas/solid chromatography and K_p is the partition coefficient, all three equations Eqs. (1)–(3) are practically the same as regards ΔS and its determination.

The experimental arrangement, on which the following theoretical analysis is based, has been published before [1–4,13,14]. For convenience it is repeated here in Fig. 1.

The necessary mathematical model pertaining to that arrangement, and used for calculating the adsorption entropy as a time-resolved quantity, can be based on *Adsorption Entropies* as described by Adamson and Gast [15]. Their relevant equation for localized adsorption with configurational entropy as the

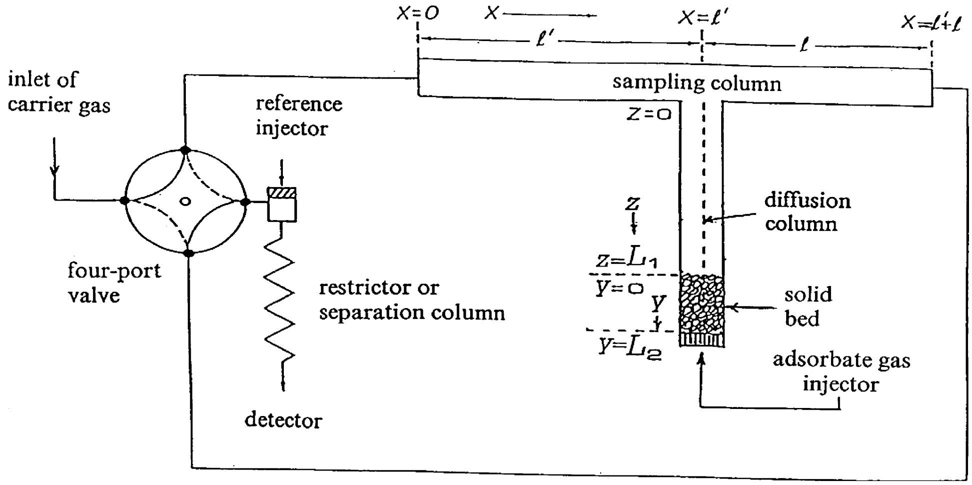

Fig. 1. Schematic representation of the columns and gas connections showing the principle for using the reversed-flow technique as an inverse gas chromatography tool.