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Adsorption, reaction and desorption rate constants, measured simultaneously by gas chromatography

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ABSTRACT

The kinetics of Gas-solid reactions can be studied in detail under non-steady state conditions, using the method of Reversed--flow Gas Chromatography. A very simple experimental set-up is required, and the mathematical equations derived permit the calculation of three rate constants simultaneously.

INTRODUCTION

Important parameters in gas-solid reactions include:

k_1 = Rate constant for adsorption of the gas reactant on the external surface of the solid reactant.

K_G = Overall mass transfer coefficient of the gas to the solid surface, related to k_1 by the equation

$$K_G = k_1 V'_G / A_s \quad (1)$$

where V'_G is the gaseous volume of void space in the solid bed, and A_s the total surface area of the solid.

k_{-1} = Rate constant for desorption of the gas reactant from the solid surface.

K_s = Overall mass transfer coefficient of the adsorbed gas in the solid, related to k_{-1} by the equation

$$K_s = k_{-1} V_s / A_s \quad (2)$$

K = Partition coefficient for the adsorption of the gas on the solid:

$$K = K_G / K_s \quad (3)$$

k_2 = Rate constant for the chemical reaction of the adsorbed gas with the solid.

All these parameters are determined simultaneously, under non--steady state conditions, with a gas chromatograph, modified as shown in Fig.1, so that the RF-GC (Reversed-Flow Gas Chromatography) technique (refs. 1-4) be applied.

METHOD

A volume of 1-2 cm^3 of the gas reactant is introduced through the injector, while an inactive carrier gas flows through the sampling column, filling also the diffusion column.

Following the reactant injection, a diffusion current of it and of the possible gaseous products, set-up inside column L_1. These currents create finite concentrations of the various gases at the junction $x = l'$, which are sampled as a function of time t_o

on reversing the direction of the carrier gas flow, by means of the valve. The flow reversals create extra peaks (sample peaks) superimposed on the continuous elution curve.

The height h of the sample peaks, when plotted as ln h vs. time t_0, gives a diffusion band, showing a maximum. In the absence of the solid, the diffusion band is determined by the diffusion coefficient of the gas reactant in the carrier gas. When the solid is present, the diffusion band is distorted in shape and/or in its slopes. It is this distortion which permits the calculation of the various parameters listed in the INTRODUCTION.

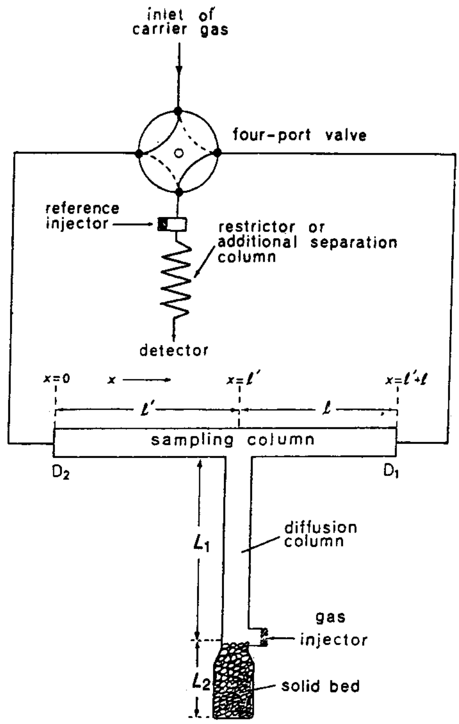

Fig.1. Outline of columns and gas connections for studying gas-solid reactions with the RG-GC technique.

The diffusion band of the gas reactant in the presence of the solid is described by the equation

$$h = N_2[(1 + \frac{Z}{Y})\exp(-\frac{X+Y}{2}\beta t_0) + (1 - \frac{Z}{Y})\exp(-\frac{X-Y}{2}\beta t_0)] \quad (4)$$

where N_2 is a constant, β is the diffusion parameter ($= \pi^2 D/L_1^2$) of the gas, determined in the absence of the solid, and X,Y,Z are given by the relations:

$$X = \pi^{-2}(\frac{1}{3} + R)^{-1} + R(\frac{1}{3} + R)^{-1}\frac{k_1}{\beta} + \frac{k_2}{\beta} + \frac{k_{-1}}{\beta} \quad (5)$$

$$(X^2 - Y^2)/4 = \pi^{-2}(\frac{1}{3} + R)^{-1}(\frac{k_2 + k_{-1}}{\beta}) + R(\frac{1}{3} + R)^{-1}\frac{k_1 k_2}{\beta^2} \quad (6)$$

$$Z = X - 2\frac{k_2 + k_{-1}}{\beta} \quad (7)$$

with R representing the ratio of the gaseous volume in vessels L_2 and L_1.

From the slopes of the diffusion band in the presence of solid reactant, the exponential coefficients $(X + Y)\beta/2$ and $(X - Y)\beta/2$ are calculated, and from these the values of X and Y. From the ratio of the two pre-exponential factors $1 - Z/Y$ and $1 + Z/Y$, the value of Z is computed. Then, X,Y and Z, so determined, are used in Eqns.5,6 and 7 to find k_1, k_2 and k_{-1}. From these rate constants, K_G, K_s and K are easily calculated using Eqs.1,2 and 3.

In conclusion, all physicochemical quantities listed in the INTRODUCTION for a gas-solid reaction can be determined under non--steady state conditions from two diffusion bands: one obtained in the absence of solid, and one with solid reactant filling vessel L_2.

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