GAS-LIQUID RATE CONSTANT MEASUREMENTS BY CHROMATOGRAPHY

J. ANDRIEU* and J.M. SMITH **

**University of California, Davis, 95616, California USA
* Université des Sciences et Techniques du Languedoc, place Eugène Bataillon, 34060 Montpellier (France)

ABSTRACT
We present an analysis for absorption and reaction of a pulse of reactant gas moving along a column containing a stationary liquid phase. For first order homogeneous reaction in the liquid film, measured moments of the effluent curve can be used to evaluate rate constants for gas-liquid reactions. This model has been applied to experimental data obtained for the absorption and reaction of carbon dioxide in aqueous \( \text{Na}_2\text{CO}_3 - \text{NaHCO}_3 \) solutions.

1 INTRODUCTION
In the past, steady-state methods have been used for determining equilibrium and rate parameters (solubilities, rate constants, diffusivities, ...) for gas-liquid process design (1); of recent industrial interest is the selective separation of acid gases by aqueous amine solutions (\( \text{SO}_2, \text{H}_2\text{S} \) or \( \text{CO}_2 \)). On the other hand, pulse response techniques have been useful for obtaining these parameters for first order and reversible adsorption processes - SMITH et col (2), (3). The objective of this communication is to apply this moment method to a chromatographic - type column in which the reacting gas flows and reacts in a stationary liquid phase.

2 THEORY
Consider a column packed with inert non-porous particles uniformly coated with absorbent liquid of thickness \( \delta \) much less than the diameter, \( d_p \), of the particles so that the liquid layer may be considered to be flat. At the interface gas and liquid phase concentrations are assumed to be in equilibrium:

In the liquid, diffusion of gaseous reactant occurs simultaneously with first order irreversible reaction

\[ A + M \stackrel{k_1}{\rightarrow} AM \]  

where AM is a non-volatile product

Concentration profile is shown in Figure 1; the column is assumed isobaric and isothermal and the gas flow through the bed is represented by the axial dispersion model (dispersion coefficient \( E_d \)).

2.1 Basic Equations

Mass conservation of A in the gas phase leads to:

\[ E_d \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} - D_A \left( \frac{\partial^2 c}{\partial x^2} \right) \bigg|_{x=\delta} = a = \frac{\partial c}{\partial t} \]  

where \( a \) is the gas-liquid interfacial area per unit volume of empty column.

Mass conservation of A in the liquid film where diffusion and reaction occur simultaneously, gives:

\[ D_A \frac{\partial^2 c}{\partial x^2} - r = \frac{\partial c}{\partial t} \]  

The reaction is assumed irreversible and first order so that the reaction rate is:

\[ r = k_1 c \]  

where \( c \) is the concentration of reactant A in the liquid.

The boundary and initial conditions for a pulse input (injection time = \( t_m \)) are:

\[ x = \delta \quad D_A \left( \frac{\partial c}{\partial x} \right) \bigg|_{x=\delta} = k_f (c_g - c_g, i) \]  

\[ x = 0 \quad c = 0 \]  

\[ z = 0 \quad c_g = 0 \text{ for } t > t_m, \quad c_g = c, g, 0 \text{ for } 0 < t < t_m \]  

\[ t = 0 \quad c_g = c = 0 \]

This system of linear equations can be solved in the Laplace domain to give \( c_g(L,s) \). Then moments, \( m_n \), of the response curve at the bed exit \( (z = L) \) may be obtained from \( c_g(L,s) \) and the limit equation:

\[ m_n = (-1)^n \lim_{s \to \infty} \frac{d^n c_g(L,s)}{ds^n} \]