

INTEGRATED RATE EQUATIONS FOR REACTION SCHEME.



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SUMMARY

From integration of the continuity equation for a plug flow, an equation which relates conversion and space time for any mechanism and rate controlling step (adsorption, surface reaction or adsorption) is calculated for the general reaction scheme $A \rightleftharpoons R+S$ carrying out in phase gas in a catalytic fixed bed reactor.

This general equation is very useful to determine kinetic constants by the integral method, or if these are known, to design the reactor.

As an example, theoretical curves of conversion vs. space time and the data experimentally obtained in the dehydrogenation of benzyl alcohol to benzaldehyde over a 20%Cu-SiO₂ catalyst are shown.

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RESUMEN

A partir de la integración de la ecuación de continuidad para un flujo de tipo pistón, se obtiene una ecuación general que relaciona la conversión alcanzada y el tiempo espacial para el esquema de reacción $A \rightleftharpoons R+S$ llevada a cabo en fase gas en un reactor catalítico de lecho fijo, válida para cualquier mecanismo y etapa controlante de velocidad (adsorción, reacción superficial o desorción).

Esta ecuación general presenta gran utilidad para la determinación de los parámetros cinéticos por el método integral, o bien si la ecuación de velocidad es conocida, para el diseño del reactor.

Como ejemplo, se muestran las curvas de conversión vs. tiempo espacial obtenidas teóricamente a partir de esta ecuación junto con los datos obtenidos experimentalmente en la deshidrogenación del alcohol bencílico a benzaldehído sobre un catalizador de 20% Cu-SiO₂.

LABURPENA

Pistoi-jarioaren jarraipen-ekuazioaren integrazioz, ohandze finkodun errektore katalitikoan eta gas fasean burututako $A \rightleftharpoons R+S$ erreakzio eskemarentzat, ukitze denbora eta lortutako trukaera erlazionatzen dituen ekuazio orokorra lortzen da, berau edozein mekanismorentzat eta abiadur etapa kontrolatzailearentzat (adsortzioa, gainazal-erreakzioa edo desortzioa) balioko izanik.

Ekuazio hau oso erabilgarria da metodo integralaren bidez konstante zinetikoak kalkulatzeko edo abiadur ekuazioa ezaguna bada errektorearen diseinurako.

Adibide gisa, ekuazio honen bidez ateratako trukaera ukitze-denborarereriko kurba teorikoak eta 20% Cu-SiO₂-zko katalisatzaile gaineko bentzil alkoholaren bentzaldehidorainoko deshidrogenazioan experimentalki lortutako datuak erakusten dira.

INTEGRATED RATE EQUATIONS FOR
REACTION SCHEME $A \rightleftharpoons R + S$

Kinetic equations for reactions catalyzed by solids based on the chemisorption mechanism may always be written as a combination of three groups:

a kinetic group: $\phi(k_i)$

a driving-force group: $\phi(x, K)$

an adsorption group: $\psi(x, K_i)$

such that the overall rate is:

$$r_A = \frac{(\text{kinetic factor}) (\text{driving-force factor})}{(\text{adsorption group})} \quad (1)$$

Summaries of these groups for various kinetic schemes are given by several authors [1,2,3].

The major part of catalytic processes in the chemical and petrochemical industry is carried out in fixed bed reactors. In these reactors, plug flow is normally assumed. The mass balance over a differential volume element for a reactant, A, involved in the reaction may be written in its integrated form as:

$$\frac{W}{F_{A0}} = \int_0^x \frac{dx}{r_A} \quad (2)$$

Integrating Eq.(2) we can get useful equations for simple reactions where the diffusion effects are negligible and the temperature and the pressure are constants.

In an earlier paper [4] we arrived at a general expression which relates the space time and the conversion for all mechanism in the reaction scheme $A \rightleftharpoons R$.

The resulting kinetic equations such as Eq.(1) where each step is rate controlling, for the overall reaction $A \rightleftharpoons R + S$,

are given in Table I. In this table are shown the kinetic equations when one or two active sites are involved in the reaction. The mechanism where the reactant A is dissociated are not analyzed.

TABLE I

Assuming that A, R and S behave like ideal gases and a feed without reaction products and carried out with n_I moles of inert per mol of A feed, the relation between the partial pressures, p_A , p_R , p_S and p_I and the conversion is found from

$$p_A = p_{A0} \frac{1-x}{1+\epsilon x} \quad (3)$$

$$p_R = p_{A0} \frac{x}{1+\epsilon x} \quad (4)$$

$$p_S = p_{A0} \frac{x}{1+\epsilon x} \quad (5)$$

$$p_I = p_{I0} \frac{1}{1+\epsilon x} = \frac{P n_I}{(1+n_I)(1+\epsilon x)} \quad (6)$$

where ϵ is the volume fractional variation, that is

$$\epsilon = \frac{V_{x=1} - V_{x=0}}{V_{x=0}} = \frac{1}{1+n_I} \quad (7)$$

All equations shown in Table I may be written in a general form as

$$r_A = \frac{D + Ex + Fx^2}{A + Bx + Cx^2} \quad (8)$$

where A, B, C, D, E and F are combined equilibrium constants, such as we can see in Table II.

TABLE II

Taking r_A expression, Eq.(8), to Eq.(2) and integrating, we arrive at,

$$\frac{W}{F_{AO}} = \int_0^x \frac{A+Bx+Cx^2}{D+Ex+Fx^2} dx =$$

$$= \frac{C}{F} x + \frac{1}{F} \left\{ \left[\left(\frac{\beta B+A}{\beta-\alpha} \right) - \frac{C}{F} \left(\frac{\beta E+D}{\beta-\alpha} \right) \right] \ln \frac{x-\beta}{-\beta} + \left[\left(\frac{\alpha B+A}{\alpha-\beta} \right) - \frac{C}{F} \left(\frac{\alpha E+D}{\alpha-\beta} \right) \right] \ln \frac{x-\alpha}{-\alpha} \right\} \quad (9)$$

where

$$\alpha = x_e \quad (10)$$

$$\beta = -x_e - \frac{K(1-\epsilon)}{K\epsilon + P_{AO}} \quad (11)$$

$$\ln \frac{x-\beta}{-\beta} = \ln \left[1 + \frac{x}{x_e + \frac{K(1-\epsilon)}{K\epsilon + P_{AO}}} \right]$$

$$\ln \frac{x-\alpha}{-\alpha} = \ln \left(1 - \frac{x}{x_e} \right)$$

With Eq.(9) we can get the values of the space time corresponding to a value of the conversion, without having to integrate, for any mechanism shown in Table I.

Equations such as the type of Eq.(9) can be used to calculate the kinetics constants by the integral method.

AN APPLICATION

The hydrogenation of benzyl alcohol into benzaldehyde, carried out in gas phase over a 20% Cu-SiO₂ catalyst at the pressure of 1 atm, has been studied by Romero et al. [5,6] resulting

the kinetic equation corresponding to the surface reaction on one active center as the rate controlling step:

$$r_A = \frac{k_{sr} K_A (p_A - p_R p_S/K)}{1 + K_A p_A + K_R p_R + K_I p_I} \quad (12)$$

The values of A, B, C, D, E and F corresponding to this controlling rate step can be found from Table II and these can be substituted in Eq.(9) to obtain the integrated equation which permit us to obtain conversion-space time curves, compare them with the experimental values and prove the validity of Eq.(12).

Romero et al [5,6] did different experiments with pure feed and using nitrogen as an inert. The calculated kinetic, equilibrium and adsorption constants were the following:

$$k_{sr} = 3.57 \cdot 10^{-5} \exp(-7189/T)$$

$$K = \exp\left(-\frac{6137}{T} + 3.91 \ln T - 11.49 - 5.55 \cdot 10^{-3} T + 8.7 \cdot 10^{-7} T^2\right)$$

$$K_A = 8.3 \cdot 10^{-3} \exp(3048.4/T)$$

$$K_R = 2.88 \cdot 10^{-9} \exp(11506.6/T)$$

$$K_S = K_I = 0$$

The resulting integrated equation is

$$\begin{aligned} \frac{W}{F_{A0}} = & \frac{1+K_R-K_A}{k_{sr} K_A (1+1/K)} x - \frac{\phi}{k_{sr} K_A p_{A0}} \\ & \left\{ \left[- \frac{1+K_I p_{I0} + p_{A0} [K_A - (2+K_I p_{I0} + K_R - K_A p_{I0})] (x_e + p_{I0} \phi)}{2x_e + p_{I0} \phi} \right] + \right. \\ & + \frac{1+K_R-K_A}{k_{sr} K_A (1+1/K)} \left(- \frac{k_{sr} K_A p_{A0} [1+p_{I0} (x_e + p_{I0} \phi)]}{2x_e + p_{I0} \phi} \right) \ln \left(1 + \frac{x}{x_e + p_{I0} \phi} \right) + \\ & + \left(\frac{1+K_I p_{I0} + p_{A0} [K_A + x_e (2+K_I p_{I0} + K_R - K_A p_{I0})]}{2x_e + p_{I0} \phi} \right) \\ & \left. + \frac{1+K_R-K_A}{k_{sr} K_A (1+1/K)} \left[\frac{k_{sr} K_A p_{A0} (1-x_e p_{I0})}{2x_e + p_{I0} \phi} \right] \ln \left(1 - \frac{x}{x_e} \right) \right\} \quad (13) \end{aligned}$$

where for simplifying we have introduced the parameter ϕ ,

$$\phi = \frac{1}{P_{A_0} (1+1/K)}$$

The relation between the constant and the conversion at equilibrium is found from:

$$K = P_{A_0} \frac{x_e^2}{1+(\epsilon-1)x_e - \epsilon x_e^2} = \frac{P_{A_0} x_e^2}{1 - P_{I_0} x_e - P_{A_0} x_e^2}$$

or

$$x_e = -\frac{\phi P_{I_0}}{2} + \sqrt{\frac{(\phi P_{I_0})^2}{4} + \phi}$$

For experiments without inert Eq.(13) is reduced to

$$\begin{aligned} \frac{W}{F_{A_0}} = & \frac{x_e^2}{k_{sr} K_A} (1 + K_R + K_A) x + \\ & + \frac{x_e}{2k_{sr} K_A} \left\{ [(1-x_e)^2 + K_A(1-x_e^2) + K_R x_e (x_e-1)] \ln\left(1+\frac{x}{x_e}\right) - \right. \\ & \left. - [(1+x_e)^2 + K_A(1-x_e^2) + K_R x_e (x_e+1)] \ln\left(1-\frac{x}{x_e}\right) \right\} \end{aligned} \quad (14)$$

Figure 1 shows the conversion-space time curves for five temperatures and for three different cases: pure feed (a), 70% of benzyl alcohol and 30% of nitrogen in the feed (b), and 30% of benzyl alcohol and 70% of nitrogen in the feed (c), calculated from Eqs. (13) and (14). The experimental points calculated by Romero et al. [5,6] are also represented in Figure 1. It can be seen a good agreement between the theoretical and the experimental values, what proves the validity of Eqs. (12), (13) and (14) for this reaction.

FIGURE 1

NOMENCLATURE

A, B, C, D, E, F	combined equilibrium constants, Table II
A, R, S, I	reactant, products and inert, respectively; benzyl alcohol, benzaldehyde, hydrogen and nitrogen in the example
F_{AO}	molar flow of reactant, mol/h
K	equilibrium constant
K_A, K_R, K_S, K_I	adsorption constants of A, R, S and I, respectively, atm ⁻¹
k_A, k_R, k_S, k_{sr}	kinetic constants
n_I	moles of I per mol of A feed
P_A, P_R, P_S, P_I	partial pressures of A, R, S and I, respectively, atm
r_A	reaction rate, moles/g cat. h
W	catalyst weight, g
x	conversion, dimensionless
x_e	conversion at equilibrium
α, β	parameters, defined in Eqs. (10) and (11)
ϵ	volume fractional, Eq. (7), dimensionless

FIGURE 1

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TABLE FOOT NOTES AND FIGURES

Table I - Kinetic equations for reaction $A \rightleftharpoons R + S$

Table II - Combined equilibrium constants for reaction
 $A \rightleftharpoons R + S$

Figure 1 - Calculated conversion-space time curves (—) and experimental values (\circ, \bullet, Δ) for: (a) pure feed, (b) 70% A and 30% I, (c) 30% A and 70% I

Rate controlling	Equation
1 active site	
Adsoption of A	$r_A = \frac{k_A (p_A - p_R p_S / K)}{1 + \frac{K_A}{K} p_R p_S + K_R p_R + K_I p_I}$
Surface reaction	$r_A = \frac{k_{sr} K_A (p_A - p_R p_S / K)}{1 + K_A p_A + K_R p_R + K_I p_I}$
Desorption of R (S is not absorbed)	$r_A = \frac{k_R K (p_A / p_S - p_R / K)}{1 + K_A p_A + K K_R p_A / p_S + K_I p_I}$
2 active sites	
Adsoption of A	$r_A = \frac{k_A (p_A - p_R p_S / K)}{1 + \frac{K_A}{K} p_R p_S + K_R p_R + K_S p_S + K_I p_I}$
Surface reaction	$r_A = \frac{k_{sr} K_A (p_A - p_R p_S / K)}{(1 + K_A p_A + K_R p_R + K_S p_S + K_I p_I)^2}$
Desorption of R	$r_A = \frac{k_R K (p_A / p_S - p_R / K)}{1 + K_A p_A + K K_R p_A / p_S + K_S p_S + K_I p_I}$
Desorption of S	$r_A = \frac{k_S K (p_A / p_R - p_S / K)}{1 + K_A p_A + K K_S p_A / p_R + K_R p_R + K_I p_I}$

TABLA 1

Rate controlling	A	B	Combinated equilibrium constants		D	E	F
			1 active site				
			C				
Adsorption of A	$1 + K_I P_{IO}$	$e(2 + K_I P_{IO}) + K_R P_{AO}$	$e(e + K_R P_{AO}) + \frac{K_A}{K} P_{AO}^2$	$K_A P_{AO}$	$D(e - 1)$	$-D(\frac{P_{AO}}{K} + e)$	
Surface reaction	$1 + K_I P_{IO} + K_A P_{AO}$	$e(2 + K_I P_{IO}) + K_R P_{AO} + (e - 1) K_A P_{AO}$	$e[e + P_{AO}(K_R - K_A)]$	$K_{SR} K_A P_{AO}$	idem	idem	idem
Desorption of R (S is not adsorbed)	$K K_R$	$1 + K_I P_{IO} + K_A P_{AO} + (e - 1) K K_R$	$e(1 - K K_R) - K_A P_{AO}$	$K_R K$	idem	idem	idem
2 active sites							
Adsorption of A	$1 + K_I P_{IO}$	$e(2 + K_I P_{IO}) + (K_R + K_S) P_{AO}$	$e[e + P_{AO}(K_R + K_S)] + P_{AO}^2 K_A / K$	$K_A P_{AO}$	idem	idem	idem
Surface reaction	$[(1 + K_I P_{IO}) + K_A P_{AO}]^2$	$2 P_{AO} (K_R + K_S) (1 + K_I P_{IO} + K_A P_{AO}) + K_A [(e - 1) - K_I P_{IO} - K_A P_{AO}] + 2e(1 + K_I P_{IO})$	$P_{AO}^2 [(K_R + K_S) - K_A]^2 + e[e + 2 P_{AO}(K_R + K_S - K_A)]$	$K_{SR} K_A P_{AO}$	idem	idem	idem
Desorption of R (or S, changing R by S)	$K K_R$	$1 + K_I P_{IO} + K_A P_{AO} + (e - 1) K K_R$	$e(1 - K K_R) + P_{AO}(K_S - K_A)$	$K_R K$	idem	idem	idem

TABLA II

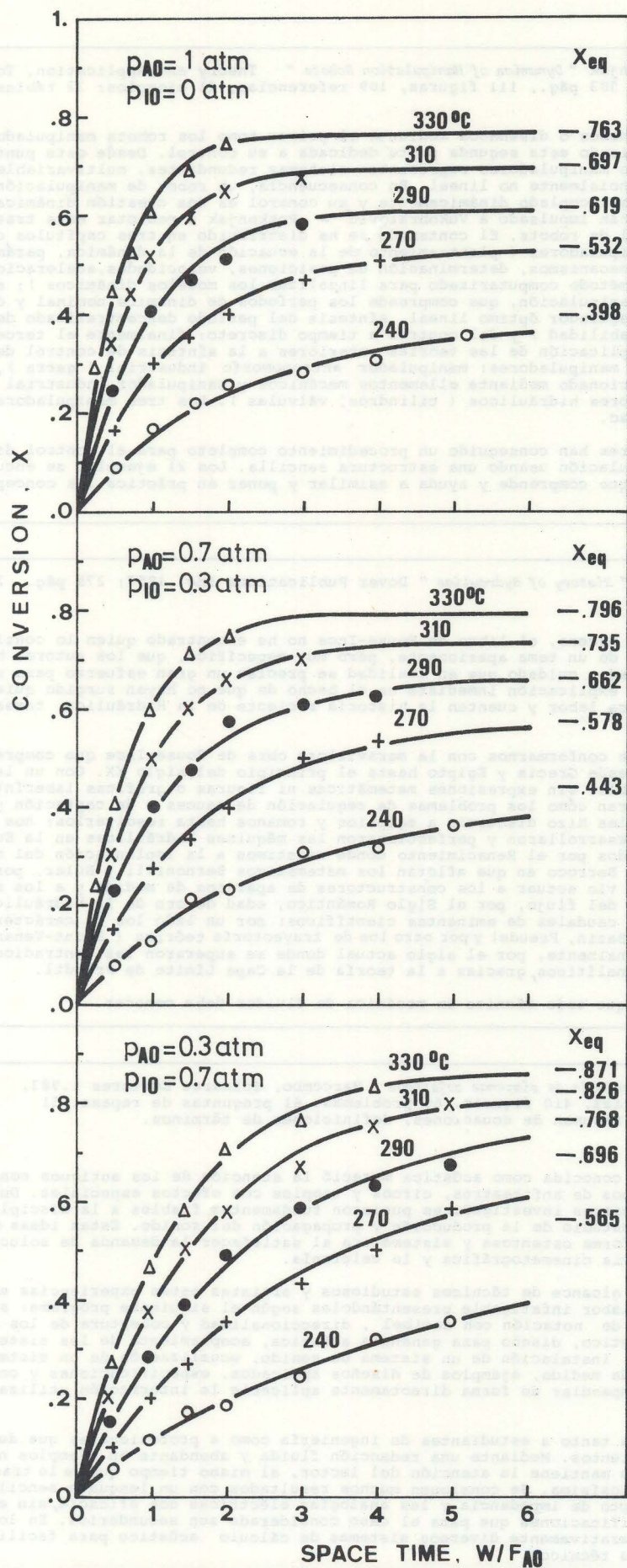


FIGURA 1