

Heterogeneous catalysis on solids of gases diffusing through a liquid layer, studied by inverse gas chromatography

John Kapolos*, Nicholas A. Katsanos

Department of Chemistry, University of Patras, 26504 Patras, Greece

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Abstract

Physicochemical parameters for heterogeneous catalytic reactions when the catalytic bed was under a liquid phase have been determined, using a non-linear adsorption isotherm by the reversed-flow version of inverse gas chromatography (RF–GC). The mathematical analysis developed in heterogeneous catalysis, mass transfer across gas–liquid boundaries, and diffusion coefficients of gases in liquids was associated with a non-linear adsorption isotherm to find the relevant equations pertaining to the problem. These equations were then used to calculate the adsorption/desorption rate constant, the rate constant for the first-order catalytic reaction and the equilibrium constant for the non-linear adsorption isotherm. The diffusion coefficients of the reactant in the liquid and gaseous phases and the partition coefficients for the distribution of the reactant between the gaseous and liquid phase were also determined.

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1. Introduction

The reversed-flow gas chromatography (RF–GC) technique, a flow perturbation method, developed in 1980 [1] and described in detail in a published book [2] has been used as a tool to study heterogeneous and homogeneous catalysis [3–8]. Also, the same technique has been used to calculate mass transfer and partition coefficients across phase boundaries, and diffusion coefficients of gases in liquids [9–15].

The aim of this paper is to develop the appropriate mathematical analysis for studying heterogeneous catalysis in the presence of a liquid phase above the catalytic bed, by using as a probe reaction the hydrogenation of 1-butene to butane over a nickel on alumina catalyst which was inside a reactor filled with liquid hexadecane.

For this purpose a combination of the mathematical analysis developed in the above cases associated with a non-linear adsorption isotherm can be employed for determining the rate constant for adsorption/desorption on the catalyst (s^{-1}), the rate constant for the first or pseudo first-order catalytic reaction (s^{-1}), and the coefficient for the non-linear adsorption isotherm ($cm^3 g^{-1} s^{-1}$).

*Corresponding author. Tel.: +30-610-996369; fax: +30-610-997144.

E-mail address: akoliadima@chemistry.upatras.gr (J. Kapolos).

2. Theory

It is known [2] that the calculation of physico-chemical parameters is based on a theoretical analysis of the diffusion band, obtained by plotting $H^{1/M}$ or $(1/M) \ln H$ against t , where H is the height of the flow reversal peaks (cm) and M (dimensionless) the response factor of the detector (1 for the linear FID) and t the time when the respective flow reversal was made.

The height H is proportional to the concentration $c(l', t)$, $H^{1/M} = gc(l', t)$, where $c(l', t)$ is the gaseous concentration of the reactant, (mol cm^{-3}), measured at the junction of the sampling column with the diffusion column (Fig. 1) and g the calibration factor for the detector, $\text{cm per mol cm}^{-3}$ [16].

The object of this section is to show how all the necessary physicochemical quantities can be extracted from the diffusion band, by solving a system of partial differential equations pertaining to regions z and y of the experimental arrangement (Fig. 1), and joined up by using appropriate boundary conditions.

2.1. Region z

Here, the gaseous concentration of the reactant c_z is given by Eq. (13) of Ref. [12] in the form of Laplace transform with respect to time (parameter p):

$$C_z = C(l', p) \cosh q_1 z + \frac{\nu C(l', p)}{D_G q_1} \sinh q_1 z - \frac{n}{a_z D_G q_1} \sinh q_1 (z - L_1) u(z - L_1) \quad (1)$$

where capital letters denote t transformed quantities with p the parameter of the transformation,

$$q_1^2 = \frac{p}{D_G} \quad (2)$$

where D_G is the gaseous diffusion coefficient of the reactant into the carrier gas, n the amount (mol) injected at $z=L_1$, a_z the cross sectional area of column z , ν the linear velocity of the carrier gas running through the sampling column, and $u(z - L_1)$ the unit step function.

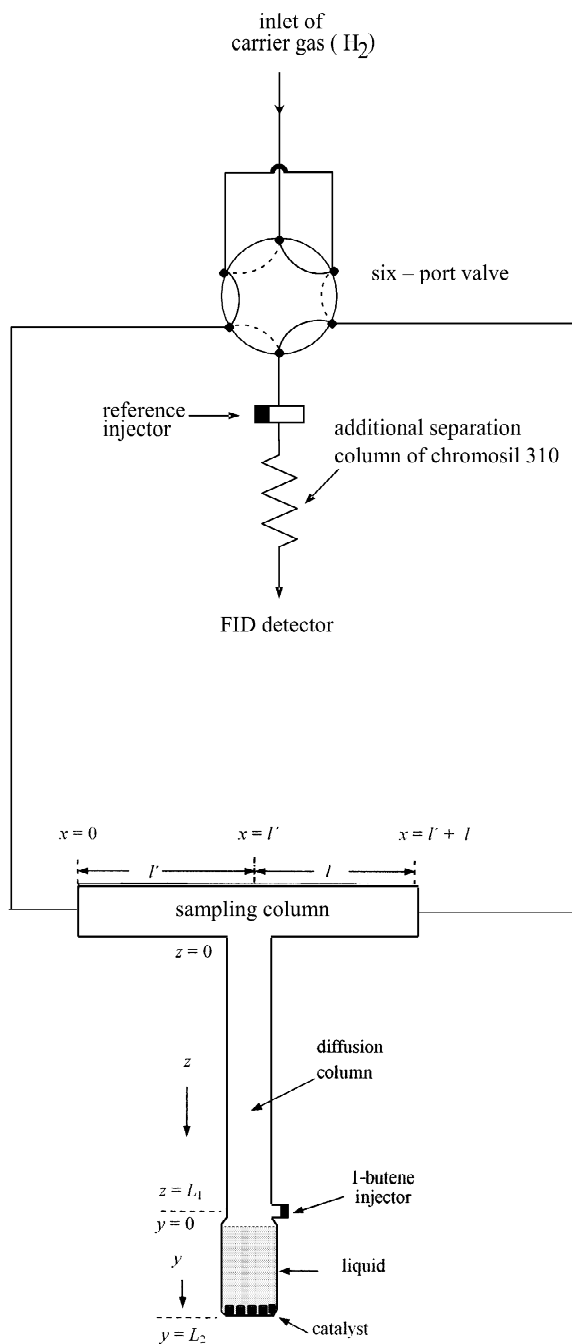


Fig. 1. Outline of the experimental arrangement used to study a heterogeneous catalytic procedure, when the catalyst is under liquid hexadecane.

2.2. Region y

In region y the liquid concentration of the reactant c_y in the form of t Laplace transformation has been found ([14] Eq. (11)) as:

$$C_y = C_y(0) \cosh q_2 y + \frac{C'_y(0)}{q_2} \sinh q_2 y \quad (3)$$

where

$$q_2^2 = \frac{p}{D_L} \quad (4)$$

D_L is the liquid diffusion coefficient of reactant, $C_y(0)$ is the t transformed function of c_y at $y=0$ and $C'_y(0) = (\partial C_y / \partial y)_{y=0}$.

Because of the presence of the catalyst bed at $y=L_2$ the boundary condition at this point is:

$$-D_L a_y \left(\frac{\partial c_y}{\partial y} \right)_{y=L_2} = k_R m (c_S^* - c_S) \quad (5)$$

where k_R = rate constant for adsorption/desorption on the solid (s^{-1}); m = total mass of the solid (g); a_y = cross-sectional area of the void space of region y (cm^2); c_S = adsorbed concentration of the reactant on the solid at time t (mol/g); and c_S^* = equilibrium adsorbed concentration of the reactant at time t (mol/g).

The rate of change of the adsorbed concentration is described by the relation:

$$\frac{\partial c_S}{\partial t} = k_R (c_S^* - c_S) - k_2 c_S \quad (6)$$

where k_2 is the rate constant (s^{-1}) for the first or pseudo first-order catalytic reaction.

By taking Laplace transforms with respect to t of Eqs. (5), (6) and then substitute C_S from the transformed Eq. (6) into the transformed Eq. (5), one obtains:

$$-D_L a_y \left(\frac{\partial C_y}{\partial y} \right)_{y=L_2} = k_R m \frac{p + k_2}{p + k_R + k_2} C_S^* \quad (7)$$

where C_S^* is the t transformed function c_S^* .

The isotherm equation is not necessary to be determined in detail as already published [16]. Only the basic definition of the local adsorption isotherm is needed, to incorporate the non-linear isotherm into the mathematical calculations. Any possible non-

linearity is automatically taken care of. The above definition is:

$$c_S^* = k_a \int_0^t c_y(\tau) d\tau \quad (8)$$

where k_a = equilibrium factor transforming into c_S^* the area under the curve of the gaseous concentration c_y in region y at any time t ($cm^3 g^{-1} s^{-1}$); and τ = dummy variable for time.

The Laplace transform of Eq. (8) with respect to time at $y=L_2$ is

$$C_S^* = k_a \frac{C_y(L_2)}{p} \quad (9)$$

and by substituting this for C_S^* in Eq. (7) there result

$$-D_L a_y \left(\frac{\partial C_y}{\partial y} \right)_{y=L_2} = k_R m \frac{p + k_2}{p + k_R + k_2} \frac{k_a}{p} C_y(L_2) \quad (10)$$

Now, $(\partial C_y / \partial y)_{y=L_2}$ and $C_y(L_2)$ are evaluated from Eq. (3) and by substituting the results in Eq. (10) the final transformed equation for region y is obtained:

$$C_y(0) [q_2 \sinh q_2 L_2 + F \cosh q_2 L_2] = -C'_y(0) \left[\frac{F}{q_2} \sinh q_2 L_2 + \cosh q_2 L_2 \right] \quad (11)$$

where F (cm^{-1}) is given by the relation

$$F = \frac{k_R m}{D_L a_y} \cdot \frac{p + k_2}{p + k_R + k_2} \cdot \frac{k_a}{p} \quad (12)$$

2.3. Linking solutions in regions z and y

Eq. (1) holding in region z is linked with Eq. (11) valid in region y, using the boundary conditions at $z=L_1$ and $y=0$:

$$K = C_y(0) / C_z(L_1) \quad (13)$$

$$a_z D_G \left(\frac{\partial C_z}{\partial z} \right)_{z=L_1} = a_y D_L \left(\frac{\partial C_y}{\partial y} \right)_{y=0} \quad (14)$$

where equilibrium Eq. (13) is assumed rapidly established with a partition coefficient K .

From Eq. (1) both $C_z(L_1)$ and $(\partial C_z / \partial z)_{z=L_1}$ are

calculated. Then, these are substituted in Eqs. (13) and (14), respectively, and the results for $C_y(0)$ and $C'_y(0)$ are substituted in Eq. (11). After omission of the term $(K \cosh q_1 L_1)$ compared with $(K\nu/D_G q_1) \sinh q_1 L_1$, and of the term $\sinh q_1 L_1$ compared with $(\nu/D_G q_1) \cosh q_1 L_1$, as was done before [6,14], and after some algebraic manipulations and rearrangements, there results:

$$C(l', p) = \frac{n}{\dot{V}} \cdot \left(\cosh q_2 L_2 + \frac{F}{q_2} \sinh q_2 L_2 \right) \cdot \left(KA \sqrt{\frac{D_L}{D_G}} \sinh q_1 L_1 \cdot \sinh q_2 L_2 + \cosh q_1 L_1 \cdot \cosh q_2 L_2 + \frac{FKAD_L}{q_1 D_G} \sinh q_1 L_1 \cdot \cosh q_2 L_2 + \frac{F}{q_2} \cosh q_1 L_1 \cdot \sinh q_2 L_2 \right)^{-1} \quad (15)$$

where $\dot{V} = a_z \nu$ is the volumetric flow-rate of the carrier gas, and $A = a_y/a_z$.

The rest of the symbols in Eq. (15) have been defined before.

Now, one expands both $\cosh qL$ and $\sinh qL$ in both factors of Eq. (15) in McLaurin series in qL , retaining only the first two terms, i.e. $\cosh qL = 1 + q^2 L^2/2$ and $\sinh qL = 0 + qL = qL$. Then, we find (leaving out extended mathematical details):

$$C(l', p) = \frac{n\alpha_G}{\dot{V}} \cdot \frac{p^3 + (\alpha_L + k)p^2 + (k\alpha_L + S\alpha_L)p + S\alpha_L k_2}{p^4 + Xp^3 + Yp^2 + Zp + W} = \frac{n\alpha_G}{\dot{V}} \cdot \frac{p^3 + (\alpha_L + k)p^2 + (k\alpha_L + S\alpha_L)p + S\alpha_L k_2}{(p - B_1)(p - B_2)(p - B_3)(p - B_4)} \quad (16)$$

In this equation

$$\alpha_G = \frac{2D_G}{L_1^2}, \quad \alpha_L = \frac{2D_L}{L_2^2}, \quad k = k_2 + k_R$$

$$\text{and } S = \frac{L_2 k_R m k_a}{D_L a_y} \quad (17)$$

whilst B_1, B_2, B_3 and B_4 are the roots of the polynomial in the denominator, related to the coefficients X, Y, Z and W and the physicochemical parameters k_R, k_a and k_2 through the equations:

$$X = \alpha_G + \alpha_L + k + \alpha_G \alpha_L G L_2 = -(B_1 + B_2 + B_3 + B_4) \quad (18)$$

$$Y = \alpha_G \alpha_L k + k\alpha_G + k\alpha_L + k\alpha_G \alpha_L G L_2 + \alpha_G Q - \alpha_L S = B_1 B_2 + B_1 B_3 + B_1 B_4 + B_2 B_3 + B_2 B_4 + B_3 B_4 \quad (19)$$

$$Z = \alpha_G \alpha_L k + \alpha_G \alpha_L Q + \alpha_G k_2 Q + \alpha_G \alpha_L S + \alpha_L k_2 S = -(B_1 B_2 B_3 + B_1 B_2 B_4 + B_1 B_3 B_4 + B_2 B_3 B_4) \quad (20)$$

$$W = \alpha_G \alpha_L Q k_2 + \alpha_G \alpha_L S k_2 = B_1 B_2 B_3 B_4 \quad (21)$$

where G and Q are given by the relations

$$G = \frac{KAL_1}{D_G} \quad \text{and} \quad Q = \frac{KAL_1 k_R m k_a}{D_G a_y} \quad (22)$$

and the rest of the symbols in Eqs. (18)–(21) having been given before.

Remembering that the height H of the extra chromatographic peaks, obtained by the repeated flow reversals, is proportional to the gaseous concentration [2] we write the inverse Laplace transforms with respect to p of Eq. (16) as:

$$H^{1/M} = gc(l', t) = A_1 \exp(B_1 t) + A_2 \exp(B_2 t) + A_3 \exp(B_3 t) + A_4 \exp(B_4 t) \quad (23)$$

where the exponential coefficients of time B_1, B_2, B_3 and B_4 satisfy Eqs. (18)–(21) while the pre-exponential factors A_1, A_2, A_3 and A_4 are independent of time and they have not any influence on the constants calculated.

3. Experimental

3.1. Apparatus

The chromatograph used was a Pye Unicam 104, with FID detector. The experimental arrangement is outlined in Fig. 1. The sampling cell consisted of the sampling column $l+l'$, the diffusion column of length L_1 , and the lower vessel of length L_2 . The branches $l=l'=60$ cm and $L_1=82.9$ – 84.1 cm were of stainless-steel chromatographic tube with 4 mm I.D., whilst vessel L_2 containing the liquid (9.9–11.1 cm) and the catalyst at its bottom of negligible height, was constructed from glass and had 17.5 mm

I.D. It was connected to the column L_1 by means of a 1/4 inch Swagelok union. The whole sampling cell was accommodated inside the oven of a usual gas chromatograph.

A six-port valve with two of its alternate ports connected by means of a 1/16 inch tube as shown, was placed inside the wall of the oven and used to connect the sampling cell to the carrier gas inlet (H_2), and to the separation column contained in the oven of another gas chromatograph and kept at 323 K, together with the flame ionization detector.

3.2. Materials

The catalyst used was a 60–65% nickel on alumina (in 3.2 mm pellets) obtained from Ventron Alfa Products.

Hexadecane, 1-butene and butane were Fluka AG “purum” products.

The carrier gas was hydrogen of 99.99% purity from Linde AG (Greece), dried by passing it through a gas purifier No. 452 of Matheson Gas Products with a flow-rate (corrected at column temperature and for pressure drop) of about $0.33 \text{ cm}^3 \text{ s}^{-1}$.

The separation column was a $2.4 \text{ m} \times 1/8$ inch Chromosil 310 purchased from Supelco SA.

3.3. Procedure

After conditioning of the catalyst by heating it in situ at 493.2 K, in the presence of a liquid, for 24 h under a continuous carrier gas flow, the oven temperature was regulated to the working one. Then 2 cm^3 (at atmospheric pressure) of 1-butene were introduced through the injector to establish constant catalytic activity.

After the chromatographic trace in the recorder had subsided to a negligible height above the baseline, a new 1 cm^3 injection of 1-butene was made. After the appearance of the continuously rising concentration–time curve, the reversing procedure for the hydrogen carrier gas flow started, each reversal lasting always 15 s. This is shorter than the gas hold-up time in the sections l and l' of the cell. Two symmetrical “sample peaks” were created by each flow reversal. One peak belonged to the reactant 1-butene and the other to the product butane. An example is given in Fig. 2. The above flow reversal

procedure was repeated many times at each temperature, giving rise to two series of sample peaks (one for reactant and one for the product), each pair of peaks corresponding to a different time from the reactant injection.

First, the diffusion coefficient of 1-butene into the carrier gas was determined by using an empty glass vessel, then by using the glass vessel filled with a liquid the diffusion and the partition coefficients of the reactant into the liquid were calculated, and finally by adding an amount of catalyst (0.49396 g) into the filled-with-the-liquid glass vessel the physicochemical coefficients for the catalytic hydrogenation of 1-butane were estimated.

In all experiments the pressure drop along the separation column was 0.58 atm, and the catalyst bed was under a pressure of 1.40–1.61 atm.

4. Calculations

These start from the experimental data obtained after injecting a small gaseous volume of the reactant (1-butene) in the absence of liquid and catalyst in region y . By using Eqs.(20) and (30) of Ref. [14], the diffusion coefficient in the gas phase D_G was calculated.

On the other hand, an injection of the reactant in the presence of liquid but in the absence of catalyst in region y , leads to the diffusion coefficient in the liquid phase D_L and the partition coefficient K for the distribution of 1-butene between the liquid and the carrier gas, using Eqs. (23), (26) and (31) of Ref. [14].

All geometrical characteristics of the cells used in these experiments are given in Table 1.

Now it was necessary to calculate the diffusion coefficients D_G , D_L and the partition coefficient K at various temperatures. A relation between the diffusion coefficients in gases and the temperature is given in [2]:

$$D_G = AT^n \quad (24)$$

where A is a constant for the same system of gases and $n=1.61$ for the diffusion in helium and $n=1.74$ for the diffusion in nitrogen. From the above equation, we can calculate the D_G values at different

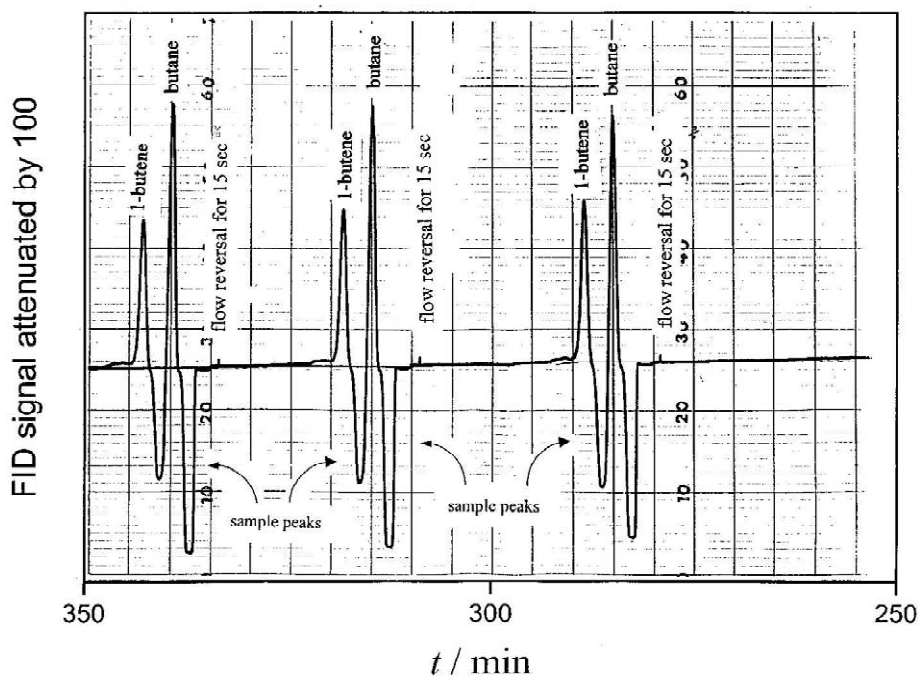


Fig. 2. Sample peaks of 1-butene and butane obtained during hydrogenation over Ni/Al₂O₃ catalyst at 383.2 K.

temperatures assuming that for hydrogen $n=1.61$ also:

$$\frac{D_{G_1}}{D_{G_2}} = \left(\frac{T_1}{T_2}\right)^n \quad (25)$$

The D_L values at different temperatures can be calculated by using the Wilke–Chang's formula [17]. The relation between D_L and T is:

$$\frac{D_{L_1}}{D_{L_2}} = \frac{T_1}{T_2} \cdot \frac{\mu_2}{\mu_1} \quad (26)$$

where μ_1 and μ_2 are the viscosity of the liquid at temperatures T_1 and T_2 , respectively.

Finally, by assuming that G in Eq. (22) is constant at different temperatures, the K values can be calculated:

$$\frac{K_1}{K_2} = \frac{D_{G_1}}{D_{G_2}} \cdot \frac{L_1}{L_2} \quad (27)$$

All results from the above calculations are given in Table 2.

In the presence of a small amount of catalyst at the bottom of vessel y , one can calculate the exponential coefficients of time B_1 , B_2 , B_3 and B_4 in Eq. (23) from the experimental values of H , t , where H is the height (in arbitrary units, say cm) of the sample

Table 1

Geometrical characteristics of the cells used to calculate diffusion coefficients D_G and D_L of 1-butene into hydrogen and hexadecane, respectively, and partition coefficient K for the distribution of 1-butene between hexadecane and hydrogen at 423.2 K

Cell no.	L_1 (cm)	L_2 (cm)	V_G (cm ³)	V'_G (cm ³)	V_L (cm ³)
1	78	–	13.533	2.37	–
2	78	10.6	13.533	2.37	25.5

The definitions for V_G , V'_G and V_L are given in Ref. [14].

Table 2

Diffusion coefficients D_G , D_L of 1-butene into hydrogen and hexadecane, respectively, and partition coefficient K for the distribution of 1-butene between hexadecane and hydrogen at various temperatures

T (K)	D_G (cm ² s ⁻¹)	D_L (10 ⁻⁵ cm ² s ⁻¹)	K
383.2	0.594	3.64	31.56
403.2	0.645	3.84	33.77
423.2	0.697	4.03	36.63

chromatographic peaks and t the respective times, when flow reversal of the carrier gas was made by using a non-linear regression analysis PC program in GW-BASIC [18].

From the values of B_1 , B_2 , B_3 and B_4 , the auxiliary coefficients X , Y , Z and W can be calculated by using Eqs. (18)–(21). From these in turn, the calculation of k_R , k_a and k_2 is carried out as follows: The sum $k_R + k_2$ is obtained from Eq. (18) in the form:

$$k = k_R + k_2 = X - \alpha_G - \alpha_L - \alpha_G \alpha_L L_2 \frac{K AL_1}{D_G} \quad (28)$$

the K and D_L having been calculated without the presence of solid catalyst as described before [14].

The product $k_R k_a$ is obtained from Eq. (19) as:

$$k_R k_a = \frac{Y - \alpha_G \alpha_L - k \alpha_G - k \alpha_L - k \alpha_G \alpha_L L_2 \frac{K AL_1}{D_G}}{\frac{\alpha_G K AL_1 m}{D_G a_y} + \frac{\alpha_L L_2 m}{D_L a_y}} \quad (29)$$

Then, by substituting the results for $k_R + k_2$ and $k_R k_a$ in Eq. (20), k_2 is calculated as follows:

$$k_2 = \frac{Z - \alpha_G \alpha_L k - \frac{\alpha_G \alpha_L K AL_1 m k_R k_a}{D_G a_y} - \frac{\alpha_G \alpha_L L_2 m k_R k_a}{D_L a_y}}{\frac{\alpha_G K AL_1 m k_R k_a}{D_G a_y} + \frac{\alpha_L L_2 m k_R k_a}{D_L a_y}} \quad (30)$$

Finally, the subtraction of k_2 from $k_R + k_2$ gives the value of k_R and the division of $k_R k_a$ by k_R gives the value of k_a . All k_2 , k_R , k_a can be substituted to W

in Eq. (21) to check the goodness of the approximation.

5. Results and discussion

The main object of this paper is to present a new mathematical model for carrying out all the necessary physicochemical measurements for studying heterogeneous catalysis in the case where the catalytic bed is under a liquid.

Using the calculation procedure outlined in the previous section, the physicochemical rate constants k_R , k_2 and the local equilibrium parameter for the adsorption isotherm, k_a are computed. All the above refer to the reactant 1-butene and are given in Table 3.

The number of significant figures in this Table is based on the standard errors of the B values. It is difficult to estimate the final errors of the calculated physicochemical parameters, since they come out as a result of a complex series of calculations and the application of the error propagation rule in a long sequence of steps does not give reliable final errors, as stated earlier [19].

It is seen from the results that the rate constant k_2 is of the same order of magnitude as that found in the absence of liquid [6], and also it changes very little with temperature. This confirms the assumption [6] that k_2 is a true rate constant for the surface reaction equal to $k_2' c_{H_2}$. As temperature rises, the adsorbed concentration c_{H_2} decreases compensating for an increase in k_2' . Also, an activation energy of 97 kJ mol⁻¹ is calculated, indicating a chemisorption process.

From the values of isotherm parameter k_a for the adsorption of 1-butene on the catalyst bed, the local isotherm can be calculated as already reported [16].

Table 3

Rate constants for adsorption/desorption (k_R), local equilibrium parameter (k_a) for the adsorption isotherm of 1-butene on the catalyst surface and rate constant (k_2) for the hydrogenation reaction at various temperatures

T (K)	k_R (10 ⁻³ s ⁻¹)	k_2 (10 ⁻⁴ s ⁻¹)	k_a (10 ⁻⁴ cm ³ s ⁻¹ g ⁻¹)
383.2	2.99	4.84	5.39
403.2	3.06	5.11	5.16
423.2	3.94	5.92	5.47

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