κ = molecular diffusivity of tracer in fluid
ξ = k_H/k_V = ratio between average permeabilities
ψ = velocity for the dispersion of a concentration front

Superscripts

(1) = quantity related to layer (1)
(2) = quantity related to layer (2)

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Kinetics of Parallel Dehydrogenation and Dehydration of Cyclohexanol on NiO-Al_2O_3 Catalyst Systems

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Although several investigators (Emelyanov et al. 1972, Rovskii et al. 1973, Ratnaswamy et al. 1970, Pillai and Kuloor 1974, Viswanathan and Yeddanapalli 1974) have studied of cyclohexanol decomposition, the reaction is more complex than had been recognized (Athappan 1979). The decomposition of cyclohexanol leading exclusively either to cyclohexene or to cyclohexanone has frequently been used as a model reaction in studying the mechanism of dehydration or dehydrogenation and in testing corresponding catalysts (Morita et al. 1970, Kuriacose et al. 1968). A quantitative study of the kinetics and mechanisms of the coupled systems, in general, where both reactions proceeded as parallel reactions has attracted little attention (Klissurskii et al. 1971, Jambor and Beranek 1975, Beranek 1975).

From the literature, it is evident that no systematic quantitative analysis of the experimental data on decomposition of cyclohexanol over NiO-Al_2O_3 system has been reported. Also, values of the rate coefficients and adsorption coefficients are unknown. Accuracy of the experimental data is of no guarantee of successful kinetic analysis when the experimental program suffers from lack of insight into the effect of different variables. Froment (1975) discussed in detail the estimation of parameters and emphasized the necessity of statistically testing the results.

In this investigation, increased emphasis is placed on model discrimination and parameter estimation. The reaction was studied at atmospheric pressure in the temperature range of 300-350°C where the homogeneous reaction was negligible. The experimental results are analyzed on the basis of Langmuir-Hinshelwood kinetics, with statistical interpretation to show the real significance of mechanism determination with precise experimental data.

CATALYST PREPARATION AND CHARACTERIZATION

Alumina supported catalysts containing up to 20 wt. % NiO were prepared by impregnating the alumina with an aqueous solution of nickel nitrate hexahydrate and dried at 110°C for 2 hours. The catalyst was then made into the cylindrical pellets, activated at 450°C for 12 hours. The entire characterization of the catalyst system by means of X-ray, i.r, d.t.a, t.g.a., electron microscopy and B.E.T. Studies has been reported elsewhere (Athappan 1979). The composition of the catalyst was chosen on the basis of Athappan's study, where it was established that the activity passed through a maximum over a catalyst composition of about 15% by weight of NiO on alumina calcined at 450°C for 12 hours. All runs in this study were performed exclusively with the catalyst of this composition (surface area = 87 m^2/g). Catalytic activity was defined as the number of moles of cyclohexanone formed/unit time/unit weight of the catalyst under the following conditions: feed liquid, pure cyclohexanol; W/F = 50 $g/(gmole)(hr)^{-1}$; cyclindrical pellets (3 mm in diameter by 3 mm in length).

APPARATUS AND PROCEDURE

The flow system with general experimental procedures and method of analysis were described by Athappan (1979). To establish the experimental conditions for which the reaction rate was not influenced by external and internal diffusion, the influence of space velocity, catalyst mass and particle size was studied as in the usual manner (Ross and Walsh 1961). As a result of these preliminary studies, the kinetic measurements were performed at flow rates from 0.57-5.7 moles hr^{-1} (N.T.P.).

The cyclohexanol was fed by the calibrated metering pump into a preheater, where it was mixed with diluent N_2 gas and vaporized. The vapor was then led to the reactor containing the catalyst bed. The temperature of the catalyst bed was measured by an iron-constantan thermocouple located in a coaxial thermowell. Temperature control was achieved by diluting the catalyst bed with inert porcelain beads, in the ratio of 1:5 by volume. The main stream of the effluents from the reactor was cooled by condenser. The liquid condensate was analyzed by gas-chromatography and the gaseous products were metered.

A 254 mm long, 12 mm diameter, copper tube packed with 20% Carbowax 20M on Chromosorb.P. (30-100 mesh) was used as an analyzing column in the chromatograph. Nitrogen was

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TABLE 1. EXPERIMENTAL FEED COMPOSITIONS

Run Numbers	Cyclohexanol (mole %)	Cyclohexanone (mole %)	Water (mole %)	Nitrogen (mole %)
1,18,35	100	—	—	—
2,19,36	10	—	—	90
3,20,37	20	—	—	80
4,21,38	30	—	—	70
5,22,39	40	—	—	60
6,23,40	90	10	—	—
7,24,41	80	20	—	—
8,25,42	70	30	—	—
9,26,43	10	10	—	80
10,27,44	20	10	—	70
11,28,45	30	10	—	60
12,29,46	20	—	80	—
13,30.47	40	—	60	—
14,31,48	60	—	40	—
15,32,49	5	—	10	85
16,33,50	10	—	10	80
17,34,51	15	—	10	75

used as a carrier gas (60 ml min^{-1} flow rate). The temperatures of the detector and injector blocks were maintained at 250°C and 220°C, respectively. The temperature of the oven was constant, at 160°C. Sample size of 1 μl was used.

After steady state was attained, a minimum of seven runs were made in 30 min. intervals. The average of the last two values of these analyses was used for the estimation of conversion. The standard deviation of the rate was less than 1.5%. The various compositions of feed for each isothermal set of runs are given in Table 1. In each case, an accurate measurement of the rate was possible, because at least one of the product was not present in the feed.

RESULTS AND DISCUSSION

The measured reaction rate data are summarized in Table 2. The partial pressures are average of inlet and outlet values. The data points in which the reaction feed was a mixture of cyclohexanol and only one other component are illustrated in Figure 1. This graph indicates that the adsorption of water has appreciable effect on the reaction rate and must be considered in any mathematical rate expression; cyclohexanone has very little effect on the rate. It is well established that, in dehydration, water has substantially greater adsorption coefficients than olefin, and in dehydrogenation, it is ketone which has greater adsorption coefficients than hydrogen (Balandin et al. 1961 Tolstopyatova et al. 1963).

Treatment of the experimental data is somewhat complicated, because of the complex nature of the coupled reaction system and the number of independent variables, that is, the four partial pressures and temperature in each reaction. Linear and nonlinear estimations were applied to various mathematical rate expressions as a method of correlating the experimental data. Based on Langmuir-Hinshelwood kinetics the models were examined with respect to experimental data, using the approach suggested by Hougen and Watson (1947). In this method, various mechanisms which might control the reaction are postulated based on single-site and two types of active sites.

MATHEMATICAL MODELLING TECHNIQUE

A nonlinear computer program utilizing the Marquardt's algorithm (Marquardt 1963, Draper and Smith 1966, Dunn and Clark 1974) was used to obtain a mathematical fit for various Hougen and Watson types of rate equations (Yang and Hougen 1950). This program minimized the residual sum of squares (RSS) during the regression. The nonlinear computer program improved basically upon the initial estimates of the various constants of the rate equation until the RSS could no longer be reduced. Approximate 95% confidence intervals for the various constants were calculated from estimates of their individual variances.

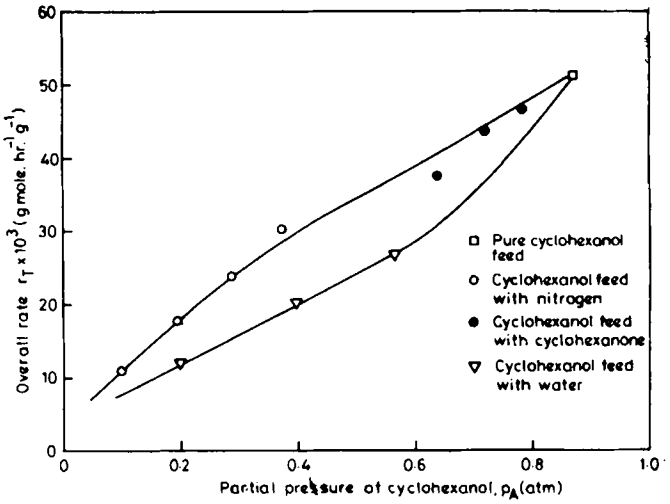

Figure 1. Partial rate data at 325°C.

Models can be rejected on the basis of negative adsorption constants or improper trends of these constants with the temperature when, in actuality, these constants are positive or have negative temperature coefficients. Of course, physical mechanisms which have such properties as adsorption constants with positive temperature coefficients are extremely rare, and if the constants of a model are actually unacceptable, the model has generally been rejected (Kittrell et al. 1965).

DATA ANALYSIS

The coupled reaction system studied has the following reaction scheme

$$C_6H_{11}OH\ (A) \xrightarrow{1} C_6H_{10}O\ (R1) + H_2\ (H)$$
$$C_6H_{11}OH\ (A) \xrightarrow{2} C_6H_{10}\ (S) + H_2O\ (W)$$

Since the differential reactor technique was employed for such runs the conversion degree always has been kept low so that the influence of reverse reactions could be neglected (Forni and Valerio 1971). Thermodynamic calculations have also shown that both the reactions are essentially irreversible ($K>10^4$). The method of Yang and Hougen (1950) was used to eliminate some of the rate controlling steps. The rate data showed that the desorption of product was not a rate controlling step.

The possible isothermal rate equations for dehydrogenation based on single and dual-site mechanisms with the use of an irreversible reaction are presented in Table 3. Similar rate expressions were used for dehydration rate data (subscripts R1 and H was replaced by S and W, respectively). These rate equations were derived with an adsorption term for each of the reaction components and diluent nitrogen. Linear and nonlinear regressions of the rate equations were made at each temperature. All possible combinations of the various adsorption terms were examined, to allow for various negligible adsorption terms. The isothermal rate equations, basic types of which are given in Table 3 resulted in 20 different mathematical forms in each case, which were confronted with the experimental data. Rate expressions were eliminated from further consideration when any of the converged adsorption constants became negative.

Table 4 gives the rate models with all positive constants which had to be retained statistically after the isothermal regressions. The converged values of the parameters of these models both by linear and nonlinear estimations are presented in Table 5. The discrimination was based upon the requirement that the kinetic and adsorption parameters had to be positive.

The data were most satisfactorily correlated by Model D14 (dual-site surface reaction with cyclohexanol adsorbed) for dehydrogenation, while the kinetics of dehydration on this catalyst could be better described by Model D13 (dual-site surface reaction with cyclohexene not adsorbed).

TABLE 2. SUMMARY OF RATE DATA

Run No.	Average Partial Pressure, atm.						Rate, g. moles $hr^{-1}g.^{-1} \times 10^3$		
	Cyclohexanol	Cyclohexanone	Hydrogen	Cyclohexene	Water	Nitrogen	r_T	r_1	r_2
1	2	3	4	5	6	7	8	9	10
				Average Temperature = 300°C					
1	0.9000	0.0162	0.0162	0.0332	0.0332	0.0000	37.5	12.2	25.3
2	0.0989	0.0003	0.0003	0.0007	0.0007	0.8992	6.4	1.8	4.6
3	0.1960	0.0008	0.0008	0.0025	0.0025	0.7973	11.6	2.9	8.7
4	0.2899	0.0023	0.0023	0.0054	0.0054	0.6950	18.1	5.4	12.7
5	0.3828	0.0041	0.0041	0.0080	0.0080	0.5926	21.7	7.2	14.5
6	0.8069	0.1280	0.0134	0.0258	0.0258	0.0000	34.0	11.6	22.4
7	0.7431	0.2049	0.0110	0.0205	0.0205	0.0000	28.9	10.1	18.8
8	0.6565	0.3019	0.0088	0.0164	0.0164	0.0000	26.0	9.0	17.0
9	0.0992	0.1001	0.0002	0.0005	0.0005	0.7994	5.1	1.4	3.7
10	0.1968	0.1006	0.0008	0.0019	0.0019	0.6981	9.4	2.9	6.5
11	0.2915	0.1025	0.0028	0.0044	0.0044	0.5945	16.6	6.5	10.1
12	0.1966	0.0005	0.0005	0.0023	0.8005	0.0000	9.8	1.8	8.0
13	0.3879	0.0021	0.0021	0.0066	0.6014	0.0000	15.2	3.6	11.6
14	0.5711	0.0042	0.0042	0.0131	0.4074	0.0000	20.6	5.1	15.5
15	0.0497	0.0001	0.0001	0.0002	0.1002	0.8498	3.6	1.1	2.5
16	0.0994	0.0002	0.0002	0.0004	0.1003	0.7996	4.0	1.1	2.9
17	0.1479	0.0003	0.0003	0.0009	0.1013	0.7490	6.0	1.4	4.6
				Average Temperature = 325°C					
18	0.8700	0.0229	0.0229	0.0421	0.0421	0.0000	51.3	18.1	33.2
19	0.0983	0.0005	0.0005	0.0009	0.0009	0.8987	10.5	3.6	6.9
20	0.1945	0.0016	0.0016	0.0029	0.0029	0.7964	15.8	5.8	10.0
21	0.2868	0.0042	0.0042	0.0060	0.0060	0.6928	23.8	9.8	14.0
22	0.3750	0.0067	0.0067	0.0112	0.0112	0.5893	31.8	11.9	19.9
23	0.7840	0.1320	0.0190	0.0324	0.0324	0.0000	45.9	17.0	28.9
24	0.7200	0.2085	0.0175	0.0272	0.0272	0.0000	41.9	16.3	25.6
25	0.6406	0.3043	0.0140	0.0205	0.0205	0.0000	36.5	14.8	21.7
26	0.0985	0.1007	0.0005	0.0009	0.0009	0.7986	9.4	3.3	6.1
27	0.1944	0.1011	0.0019	0.0026	0.0026	0.6980	13.7	4.7	9.0
28	0.2899	0.1025	0.0029	0.0054	0.0054	0.5973	19.5	6.9	12.6
29	0.1958	0.0009	0.0009	0.0027	0.7997	0.0000	12.3	2.9	9.4
30	0.3842	0.0029	0.0029	0.0084	0.6017	0.0000	19.9	5.1	14.8
31	0.5637	0.0057	0.0057	0.0162	0.4087	0.0000	26.4	6.9	19.5
32	0.0497	0.0001	0.0001	0.0003	0.1003	0.8499	5.1	1.5	3.6
33	0.0989	0.0003	0.0003	0.0007	0.1006	0.7922	6.9	2.2	4.7
34	0.1475	0.0007	0.0007	0.0015	0.1018	0.7480	9.8	2.9	6.9
				Average Temperature = 350°C					
35	0.8467	0.0303	0.0303	0.0464	0.0464	0.0000	62.2	24.6	37.6
36	0.0974	0.0009	0.0009	0.0015	0.0015	0.8979	16.4	5.8	10.6
37	0.1917	0.0028	0.0028	0.0042	0.0042	0.7944	24.3	9.8	14.5
38	0.2825	0.0055	0.0055	0.0079	0.0079	0.6905	31.8	13.3	18.8
39	0.3685	0.0094	0.0094	0.0130	0.0130	0.5864	40.5	17.0	23.5
40	0.7661	0.1362	0.0246	0.0365	0.0365	0.0000	55.7	22.4	33.3
41	0.7044	0.2118	0.0222	0.0308	0.0308	0.0000	51.0	21.3	29.7
42	0.6247	0.3066	0.0191	0.0248	0.0248	0.0000	47.4	20.6	26.8
43	0.0977	0.1006	0.0008	0.0013	0.0013	0.7983	14.5	5.4	9.1
44	0.1930	0.1016	0.0022	0.0037	0.0037	0.6959	20.2	7.6	12.6
45	0.2866	0.1036	0.0043	0.0067	0.0067	0.5922	25.7	10.1	15.6
46	0.1940	0.0012	0.0012	0.0037	0.8000	0.0000	17.3	4.3	13.0
47	0.3822	0.0033	0.0033	0.0095	0.6018	0.0000	22.4	5.8	16.6
48	0.5614	0.0063	0.0063	0.0171	0.4089	0.0000	28.2	7.6	20.6
49	0.0494	0.0002	0.0002	0.0004	0.1004	0.8495	7.9	2.5	5.4
50	0.0985	0.00005	0.0005	0.0010	0.1008	0.7989	9.8	3.3	6.5
51	0.1464	0.0010	0.0010	0.0022	0.1022	0.7473	14.1	4.7	9.4

The effect of temperature on the rate expressions was introduced by substituting the Arrhenius temperature dependency relation for each of the parameters

$$K_i = A^\circ e^{-\Delta E/RT}$$

The model D14 for dehydrogenation then becomes

$$r_1 = \frac{A^\circ e^{-\Delta E_1/RT} \cdot K_A^\circ e^{-\Delta E_A/RT} \cdot P_A}{[1 + K_A^\circ e^{-\Delta E_A/RT} \cdot P_A]^2}$$

Similarly, for dehydration model D13 becomes

$$r_2 = \frac{A^\circ e^{-\Delta E_1/RT} K_A^\circ e^{-\Delta E_A/RT} \cdot P_A}{[1 + K_A^\circ e^{-\Delta E_A/RT} P_A + K_W^\circ e^{-\Delta E_W/RT} \cdot P_W]^2}$$

The converged values of the parameters of these expressions are given in Table 6. The values of activation energies for the adsorption term are negative, indicating a satisfactory temperature relationship. The ΔE_1 is positive as would be expected.

The apparent activation energies for dehydrogenation and dehydration are 28.6 and 12.4 kcal $mole^{-1}$, respectively, in agreement with the values reported by Vishwanathan and Yaddanapalli (1974). This indicates that one of the effects of NiO in Al_2O_3 may be the physical coverage of the surface, resulting in the loss of surface for the dehydration of cyclohexanol and promotion of a competitive dehydrogenation reaction.

These results indicate that dehydrogenation and dehydration proceed on different sites of the catalyst. Nevertheless, a com-

TABLE 3. POSSIBLE ISOTHERMAL RATE EQUATIONS

Reaction: $C_6H_{11}OH$ (A) $\xrightarrow{1}$ $C_6H_{10}O$ (R1) + H_2 (H); $C_6H_{11}OH$ (A) $\xrightarrow{2}$ C_6H_{10} (S) + H_2O (W)

Inert:Nitrogen (N)

A. Single-Site Mechanism

Rate Controlling Step	*Rate Equation*
a. Adsorption of cyclohexanol	$K_1K_AP_A/(1 + K_{R1}P_{R1} + K_HP_H + K_NP_N)$
b. Surface reaction	$K_1K_AP_A/(1 + K_AP_A + K_{R1}P_{R1} + K_HP_H + K_NP_N)$

B. Dual-Site Mechanism

Rate Controlling Step	*Rate Equation*
a. Adsorption of Cyclohexanol *A*	$K_1K_AP_A/(1 + K_{R1}P_{R1} + K_HP_H + K_NP_N)$
b. Surface reaction	$K_1K_AP_A/(1 + K_AP_A + K_{R1}P_{R1} + K_HP_H + K_NP_N)^2$

TABLE 4. MODELS REMAINING AFTER ISOTHERMAL REGRESSION.

Reaction: $C_6H_{11}OH$ (A) $\xrightarrow{1}$ $C_6H_{10}O$ (R1) + H_2 (H); $C_6H_{11}OH$ (A) $\xrightarrow{2}$ C_6H_{10} (S) + H_2O (W)

Inert:Nitrogen (N)

Model	Rate Controlling Step	Rate Equation: Dehydrogenation	Rate Equation: Dehydration
S13	Single-site surface reaction with cyclohexene (S) not adsorbed	—	$\frac{K_1K_AP_A}{(1 + K_AP_A + K_WP_W)}$
S14	Single-site surface reaction with cyclohexanol (A) adsorbed	$\frac{K_1K_AP_A}{(1 + K_AP_A)}$	$\frac{K_1K_AP_A}{(1 + K_AP_A)}$
D13	Dual-site surface reaction with cyclohexene (S) not adsorbed	—	$\frac{K_1K_AP_A}{(1 + K_AP_A + K_WP_W)^2}$
D14	Dual-site surface reaction with cyclohexanol (A) adsorbed	$\frac{K_1K_AP_A}{(1 + K_AP_A)^2}$	$\frac{K_1K_AP_A}{(1 + K_AP_A)^2}$

TABLE 5. ISOTHERMAL REGRESSION

Model	Temp., (°C)	$K_1 \times 10^3$ (g moles $hr^{-1}g^{-1}$) Linear	$K_1 \times 10^3$ (g moles $hr^{-1}g^{-1}$) Non-linear	K_A(atm^{-1}) Linear	K_A(atm^{-1}) Non-linear	K_W(atm^{-1}) Linear	K_W(atm^{-1}) Nonlinear	Avg. Abs. % Error Linear	Avg. Abs. % Error Non-Linear	RSS Linear	RSS Non-linear
					Dehydrogenation						
S14	300	118.7	117.6 ± 2.0	0.11	0.12 ± 0.27			15.2	5.78	0.60×10^3	0.37×10^{-4}
	325	56.0	106.0 ± 4.0	0.45	0.23 ± 0.34			2.4	3.30	0.36×10^3	0.11×10^{-3}
	350	42.0	206.3 ± 7.0	0.98	0.42 ± 0.40			0.34	4.70	0.86×10^2	0.31×10^{-3}
D14	300	98.9	81.7 ± 4.4	0.43	0.20 ± 0.16			0.02	3.60	0.42×10^1	0.38×10^{-4}
	325	119.3	231.8 ± 4.7	0.21	0.10 ± 0.15			0.15	3.04	0.21×10^1	0.11×10^{-3}
	350	203.0	759.1 ± 8.0	0.07	0.03 ± 0.35			4.10	3.90	0.47×10^1	0.31×10^{-3}
					Dehydration						
S13	300	52.3	57.0 ± 4.0	0.86	0.80 ± 0.20	1.21	0.3 ± 0.8	1.60	2.50	0.12×10^4	0.43×10^{-4}
	325	63.5	77.0 ± 5.0	0.97	0.75 ± 0.13	0.08	0.37 ± 0.9	6.00	3.60	0.27×10^3	0.76×10^{-4}
	350	55.0	60.0 ± 9.0	1.75	1.47 ± 0.40	0.51	0.83 ± 0.3	8.40	3.00	0.37×10^3	0.14×10^{-3}
S14	300	43.4	58.3 ± 3.0	1.34	0.72 ± 0.16			7.50	1.20	0.30×10^3	0.48×10^{-3}
	325	65.0	85.6 ± 10.0	0.92	0.62 ± 0.34			14.00	3.30	0.26×10^3	0.78×10^{-4}
	350	54.5	64.8 ± 8.0	1.66	1.25 ± 0.33			7.50	2.90	0.31×10^3	0.18×10^{-3}
D13	300	140.0	107.0 ± 4.0	0.66	0.41 ± 0.08	0.20	0.44 ± 0.31	0.17	2.12	0.62×10^1	0.43×10^{-4}
	325	146.0	167.0 ± 5.0	0.42	0.35 ± 0.04	0.05	0.32 ± 0.16	1.10	2.80	0.31×10^1	0.78×10^{-4}
	350	164.0	258.0 ± 9.0	0.31	0.29 ± 0.13	0.02	0.30 ± 0.23	0.41	3.50	0.54×10^1	0.14×10^{-2}
D14	300	118.0	141.4 ± 3.0	0.46	0.29 ± 0.06			0.19	0.80	0.47×10^1	0.49×10^{-4}
	325	149.0	200.0 ± 4.0	0.41	0.26 ± 0.07			1.02	1.60	0.31×10^1	0.80×10^{-4}
	350	135.0	166.7 ± 6.0	0.65	0.45 ± 0.09			0.40	4.20	0.53×10^1	0.19×10^{-3}

TABLE 6. CONVERGED VALUES OF THE PARAMETERS

Parameter	Estimate
D14-Dehydrogenation	
A_1	5.35×10^9
ΔE_1	28.66 kcal (g.mole^{-1})
K_A°	2.8×10^{-8}
ΔE_A	-17.89 kcal (g.mole^{-1})
D13-Dehydration	
A_1°	4.5×10^3
ΔE_1	12.4 kcal (g.mole^{-1})
K_A°	1.3×10^{-2}
ΔE_A	-3.87 kcal (g.mole^{-1})
K_W°	8.7×10^{-4}
ΔE_W	-8.91 kcal (g.mole^{-1})

parison of adsorption coefficients of cyclohexanol for these two reactions show that primary interaction of the cyclohexanol is rather non-specific. It might take place on surface sites which are not identical with reaction centers participating in further transformation of adsorbed cyclohexanol. This primary interaction could be of physical character (Jambor and Beranek 1975, Beranek 1975). Physical character of the adsorption of the reaction components is at least partially indicated, also, by the fact that the gaseous component (hydrogen) does not influence the reaction, while other (water) does. This assumption could explain why water retards the reaction by which it is formed.

NOTATION

A = cyclohexanol
A° = frequency factor
F = feed rate of cyclohexanol, (g.moles)/(hr)
H = hydrogen
K_1 = rate constant, (g.moles)/(hr)(g)
K_i = adsorption equilibrium constant for component, i, atm^{-1}
K_1° = Arrhenius adsorption constant for component i, atm^{-1}
n = total number of data points
P_i = partial pressure of component i, atm
$R1$ = cyclohexanone
R = gas constant, (cal)/(g.mole)(°K)
r = experimental reaction rate, (g.moles)/(hr)(g)
$\hat{r}$ = calculated reaction rate, (g.moles)/(hr)(g)
r_1 = dehydrogenation rate, (moles of cyclohexanone formed)/(hr)(g)
r_2 = dehydration rate, (moles of cyclohexene formed)/(hr)(g)
r_T = $r_1 + r_2$
S = cyclohexene
T = absolute temperature, °K
W = water
W = weight of catalyst, g
ΔE_1 = activation energy for rate constant, (k.cal)(g.mole)
ΔE_i = activation energy for adsorption of component i, (k.cal)/(g.mole)

Definitions

$$RSS = \sum_{i=1}^{n} (r_i - \hat{r}_i)^2$$

$$\sigma^2 = \sum_{i=1}^{n} (r_i - \hat{r}_i)^2 / DF$$

Avg. Abs. per cent error

$$= \frac{1}{n}\left[\sum_{i=1}^{n} \frac{r_i - \hat{r}_i}{r_i}\right] \times (100)$$

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