Catalytic Butene Isomerization

CHEMICAL ENGINEERING KINETICS OF DOUBLE BOND MIGRATION

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The double bond migration in *n*-butene over an alumina catalyst at 482° to 752° F. was investigated at butene flow rates of 0.19 to 3.38 pound-moles per square foot of catalyst cross section per hour (space velocities of 400 to 7100 hour^{-1}). The experimental data were readily correlated by plotting the height of a reactor unit, H_r, versus the butene flow rate at each temperature. H_r, defined by the expression $H_r = \frac{Z}{\ln\left(\frac{y_1 - y^*}{y_2 - y^*}\right)}$, is shown by mathematical treatment to be a linear function of the gas flow rate at a constant temperature and, for the flow rate range studied, the data verify this conclusion. From a consideration of the Arrhenius equation, it is shown that log H_r should be approximately a linear function of $1/T$ for a constant gas velocity. This relation is found experimentally to hold between 482° and 752° F. For this reaction the rate-controlling step is the surface reaction, but the theoretical treatment shows that the linear relation between H_r and the flow rate should hold for any reversible reaction of apparent first order in both directions.

A METHOD is needed which a chemical engineer can apply to data obtained in a small-scale catalytic reactor and estimate the dimensions of a reactor required for a much larger unit which perhaps will be operating under different conditions of temperature and space velocity. It is the purpose of this work to demonstrate that for a reversible reaction of apparent first order in both directions such an extrapolation, within certain limitations, should be possible.

Hougen and Watson (*7*) developed general rate equations for chemical reactions catalyzed by solids. They considered the effects of the usual variables and the relative effects of the several steps involved in the over-all reaction. Their equations were applied to the hydrogenation of iso-octene by Beckman, Pufahl, and Hougen (*1*) and to the dehydrogenation of *n*-butane by Dodd and Watson (*6*). Their equations, however, are not simple to use and contain constants difficult to evaluate.

Hurt (*8*) reviewed the previously published literature which he considered useful for chemical engineering design calculations. He suggested that the "transfer unit" concept frequently applied to adsorption and distillation calculations could be extended to some catalyzed chemical reactions. He made use of three fundamental equations:

$$H_t = \frac{dZ}{\frac{-dy}{y - y_i}} = \text{height of a transfer unit} \quad (1)$$

$$H_c = \frac{dZ}{\frac{-dy}{y_i - y^*}} = \text{height of a catalyst unit} \quad (2)$$

$$H_r = \frac{dZ}{\frac{-dy}{y - y^*}} = \text{height of a reactor unit} \quad (3)$$

where Z is the catalyst bed depth, y is the mole fraction of reactant at any point in the gas stream, y_i is the corresponding mole fraction of reactant on the catalyst surface, and y^* is the equilibrium mole fraction of reactant.

Assuming these relations to be true, he showed that

$$H_r = H_c + H_t \quad (4)$$

In the present work the isomerization of 1-butene to 2-butene was followed experimentally in order to test further the applicability of such equations to a catalytic system. Coull and Bishop (*5*) modified this concept when correlating data obtained in the synthesis of butadiene from alcohol.

BUTENE ISOMERIZATION APPARATUS

The equipment consisted essentially of an arrangement of apparatus, shown schematically in Figure 1, designed to supply reactant and diluent gases at a known constant rate, a catalyst bed whose temperature is precisely and uniformly controlled, and a system of receivers to collect, measure, and separate the product from the diluent gases. A high vacuum system was provided to pump adsorbed gases from the catalyst surface.

The furnace was constructed with individually controlled heaters placed so as to minimize the longitudinal temperature gradients caused by heat losses at the ends of the furnace. These consisted of a 420-watt continuous heater and a 150-watt intermittent heater wound along the length of the aluminum core, and two 220-watt heaters wound along 6-inch sections of the core, one at each end of the furnace. Each of the four heaters was individually controlled by a variable transformer. The temperature was controlled through utilization of the thermal expansion of the aluminum furnace core as indicated in Figure 2. Two thirds of the length of the 3-foot furnace could be held within a temperature range of 2° F. with a fluctuation at any point of no more than ±0.2° F.

The catalyst bed comprised a cylindrical layer of $^3/_{32}$-inch alumina pellets, 2 inches deep and 1 inch in diameter, placed at the center of the furnace. The catalyst temperature was measured by a sliding thermocouple contained in a 7-mm. outside diameter glass tube passed lengthwise through the center of the catalyst bed.

BUTENE AND CATALYSTS

The pure grade 1-butene was used as purchased with no further purification except passage through a drying train containing Drierite and activated alumina. Spectroscopic analysis indicated that the material was at least 98% 1-butene, with small amounts of 2-butene, the butanes, and traces of other hydrocarbons also present.

The catalyst used was a pelleted alumina catalyst. Prior to use as a catalyst, it was washed with 1 *N* hydrochloric acid and vacuum dried at 570° F. The acid wash reduced the amount of sodium in the catalyst. Spectroscopic analysis indicated that calcium and iron were present in amounts less than 0.1%, along with traces, less than 0.01%, of several other constituents.

The surface area of the alumina was calculated by the Brunauer-Emmett-Teller method (*3*) to be 195 square meters per gram.

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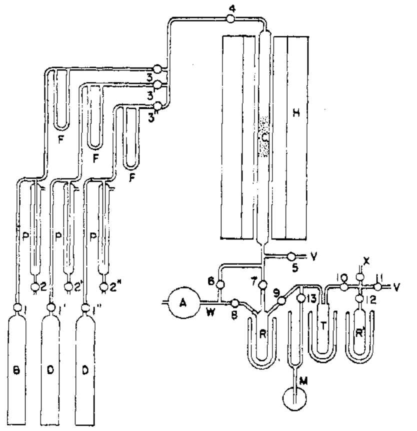

Figure 1. Butene Isomerization Apparatus

A. Wet test meter
B. Butene supply
C. Catalyst bed
D. Diluent gases
F. Flowmeter
H. Furnace
M. Manometer
P. Pressure regulator
R. Receiver
T. Dry ice-acetone trap
V. Vacuum line
W. Waste line
X. Vapor pressure analyzer

The nitrogen isotherm obtained at −319° F. indicated that the catalyst had a wide pore size distribution.

ANALYTICAL METHOD

All samples were analyzed by means of the infrared spectroscope using a modification of the technique described by Brattain, Rasmussen, and Cravath (*2*). This procedure and the apparatus have been described by Coggeshall and Saier (*4*). Vapor pressure measurements were made on the samples produced at the higher temperatures in order to detect possible cracking.

VARIATION OF H_r WITH FLOW RATE

A series of butene isomerization runs were made at temperatures varying from 482° to 752° F. and at butene flow rates from 0.19 to 3.38 pound-moles per square foot of catalyst cross section per hour. All other variables were held as constant as possible by using pure 1-butene feed, a single batch of catalyst for all runs, and operating at atmospheric pressure.

The most significant variable proved the most difficult to control. The catalytic activity of the single alumina catalyst sample used for all of the isomerization experiments changed little during a series of runs made during one day, but sometimes changed appreciably over a period of several days, depending on the treatment of the catalyst.

Since the catalyst activity could not be readily controlled, the data obtained in all runs were corrected for the changing activity of the catalyst. These corrections were made by use of "standard runs" which were made at 572° F. and at a butene flow rate of 0.18 lb.-moles/(sq. ft.) (hr.). The standard runs were made before and after each series of runs made at any other set of conditions. These were then used to correct the catalyst activity to that of the standard catalyst which in the standard run gave a value for H_r of 2.20 which corresponds to a conversion of about 50%. For example, by applying Equation 17, the integrated form of Equation 3,

$$H_r = \frac{2}{2.303 \log \dfrac{1.0 - 0.136}{0.764 - 0.136}} = 6.27$$

in the first experiment cited in Table I. However, H_r for the standard runs made at 572° F. before and after the series at 482° F. averaged 2.41 as compared with 2.20 for the standard activity. Hence, all H_r values for this series are multiplied by the ratio 2.20/2.41 and the corrected value of H_r in this example becomes 5.72. This procedure was tested by comparing two series of runs made at 572° F.; in one of these the catalyst showed the standard activity and in the other it was about 100% more active; this was far the greatest deviation from the standard activity shown by the catalyst at any time during these experiments. A plot of H_r versus flow rate for these runs, as shown by the squares and triangles of the 572° F. plot in Figure 3, after correcting for the changed activity of the catalyst by means of the standard runs made before and after the second series, shows the two curves to be superimposed. Hence, this correction seems to be justified.

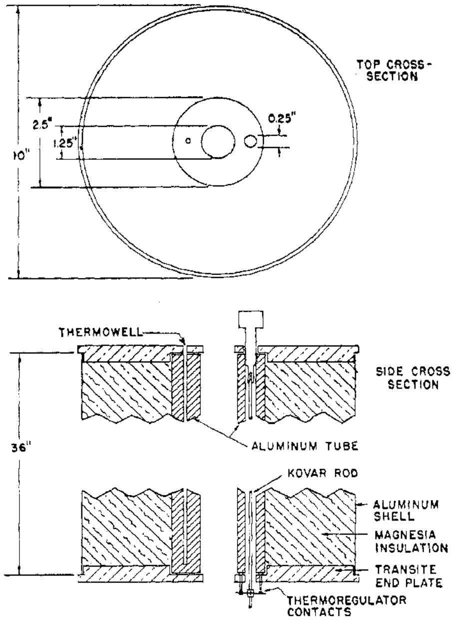

Figure 2. Details of Furnace Construction

The data for all runs made under the several sets of conditions were thus corrected for any change in the catalyst activity at 572° F. The value of H_r was calculated by means of Equation 17. The equilibrium amounts of 1-butene at the various temperatures were calculated from the free energy computations published by Thacker, Folkins, and Miller (*10*). The experimental values published subsequently by Voge and May (*11*) are in substantial agreement with these. The calculated equilibrium amounts of the *n*-butene as a function of temperature are shown in Figure 4.

The data in Table I were readily correlated by plotting H_r versus the flow rate for each temperature. The resulting curves shown in Figure 3 were in every instance linear. An examination of the term H_r will show that this result is to be expected. Equations 1, 2, and 3 can be derived by a semiempirical approach similar to that used when applying the transfer unit concept to distillation. Equation 3, which is useful for correlating these isomerization data, can be derived rigorously.

Consider a differential length, dZ, of a catalyst bed through which a gas mixture is flowing. If y is the mole fraction of the reactant under consideration at any point in the fluid stream moving through the catalyst section, the rate of disappearance of the reactant from the fluid stream at that point is given by

$$-\frac{dy}{dt} = -\frac{dy}{dZ}\frac{dZ}{dt} \qquad (5)$$

TABLE I. BUTENE ISOMERIZATION DATA

Temperature, ° F.	Butene Flow Rate, Lb.-Moles/(Sq. Ft.)(Hr.)	Conversion to 2-Butene, % $(1 - y_2)$	H_r Values[a]	y^*	Average[b] H_r for Standard Runs at 572° F.	H_r Corrected to Standard Catalyst Activity
481.8	0.194	23.6	6.27	0.136	2.41	5.72
481.5	0.386	13.2	12.06	0.136	2.41	11.01
482.2	0.580	8.2	20.62	0.136	2.41	18.73
482.4	0.774	7.5	22.00	0.136	2.41	20.08
482.2	0.969	6.2	26.85	0.136	2.41	24.51
481.1	1.545	4.5	37.42	0.136	2.41	34.16
482.7	0.194	24.4	6.03	0.136	2.41	5.50
526.8	0.387	20.4	7.29	0.150	2.39	6.71
525.6	0.583	15.1	10.23	0.150	2.39	9.42
525.6	0.775	11.4	13.89	0.150	2.39	12.79
525.4	0.968	9.9	16.04	0.150	2.39	14.76
529.5	1.545	6.2	26.43	0.150	2.39	24.33
527.2	0.194	44.6	2.69	0.150	2.39	2.48
572.5	0.392	33.2	3.95	0.164	2.20	3.95
571.6	0.585	24.5	5.76	0.164	2.20	5.76
572.5	0.775	18.9	7.80	0.164	2.20	7.80
572.2	0.968	15.9	9.48	0.164	2.20	9.48
571.6	1.549	11.3	13.77	0.164	2.20	13.77
572.2	0.197	50.0	2.19	0.164	2.20	2.19
572.0	0.192	70.6	1.07	0.164	1.06	2.22
572.4	0.386	55.6	1.83	0.164	1.06	3.80
571.4	0.582	44.0	2.68	0.164	1.06	5.56
572.0	0.773	34.7	3.73	0.164	1.06	7.74
570.9	0.967	30.9	4.33	0.164	1.06	8.99
572.4	0.192	71.3	1.04	0.164	1.06	2.16
617.7	0.192	68.9	1.11	0.175	1.55	1.58
615.6	0.394	56.0	1.76	0.175	1.55	2.50
615.0	0.584	39.0	3.12	0.175	1.55	4.43
615.7	0.782	32.5	3.99	0.175	1.55	5.66
617.9	1.014	26.4	5.18	0.175	1.55	7.35
617.2	1.552	18.9	7.68	0.175	1.55	10.90
615.4	0.194	66.7	1.21	0.175	1.55	1.72
663.3	0.195	69.6	1.03	0.187	1.61	1.41
661.4	0.386	50.8	2.04	0.187	1.61	2.79
661.1	0.582	45.2	2.46	0.187	1.61	3.36
661.1	0.784	37.5	3.23	0.187	1.61	4.41
661.1	0.968	31.6	4.06	0.187	1.61	5.55
660.7	1.544	21.9	6.37	0.187	1.61	8.70
660.7	0.197	66.8	1.16	0.187	1.61	1.59
705.9	0.397	67.9	1.10	0.198	1.73	1.40
708.4	0.584	60.2	1.44	0.198	1.73	1.83
705.6	0.788	48.3	2.17	0.198	1.73	2.76
706.8	0.975	42.0	2.70	0.198	1.73	3.43
705.2	1.212	34.5	3.56	0.198	1.73	4.53
705.9	1.401	33.7	3.67	0.198	1.73	4.67
706.3	1.547	30.8	4.13	0.198	1.73	5.25
704.8	0.197	74.8	0.74	0.198	1.73	0.94
751.1	0.194	76.0	0.55	0.219	2.03	0.60
753.3	1.544	41.2	2.67	0.219	2.03	2.89
752.9	1.235	42.8	2.52	0.219	2.03	2.73
752.5	1.048	47.2	2.16	0.219	2.03	2.34
752.9	0.966	49.2	2.01	0.219	2.03	2.18
753.1	0.788	54.4	1.68	0.219	2.03	1.82
751.1	0.575	62.6	1.24	0.219	2.03	1.34
753.8	0.381	66.2	1.06	0.219	2.03	1.15

[a] $H_r = \dfrac{2}{2.303 \log \dfrac{1.0 - y^*}{y_2 - y^*}}$.

[b] These values are calculated from the butene conversions in the standard runs at 572° F. The following values are, respectively, H_r calculated from the standard run or runs made before the given series, the average H_r (underlined) listed above, and the H_r calculated from the standard run or runs made after the given series: 2.37, 2.41, 2.40, 2.49; 2.39, 2.39, 2.39; 2.14, 2.26, 2.20, 2.20; 1.07, 1.06, 1.05; 1.26, 1.55, 1.83; 1.56, 1.61, 1.65; 1.63, 1.84, 1.73, 1.73; 2.04, 2.03, 2.02.

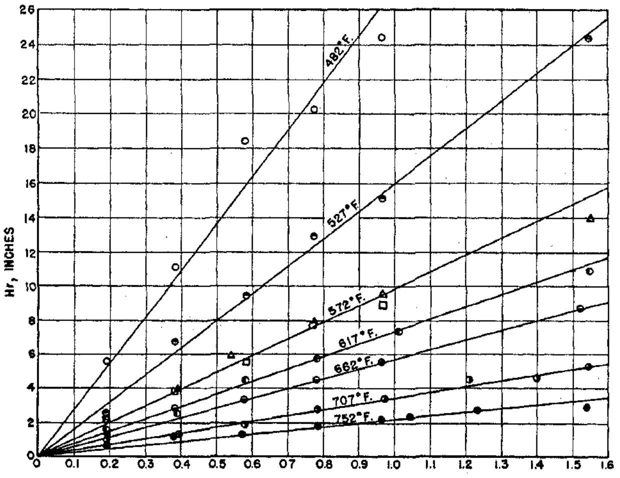

Figure 3. Relation between H_r and Flow Rate at Various Temperatures

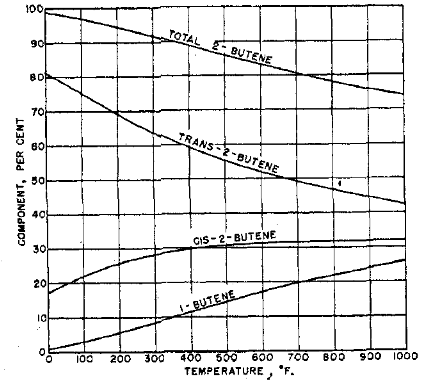

Figure 4. Equilibrium among the Normal Butenes

For convenience, dZ/dt, the superficial linear velocity, is defined as being equal to a term F, and Equation 5 is rewritten

$$dZ = F \frac{dy}{\frac{dy}{dt}} \tag{6}$$

By integrating,

$$Z = F \int \frac{dy}{\frac{dy}{dt}} \tag{7}$$

In order to integrate Equation 7 further, the term dy/dt must be evaluated by examining the physical conditions involved. If one assumes that the catalytic reaction involves two over-all steps—transport of the reactant to the catalyst and the actual reaction at the surface—there are three possible cases:

I. The surface reaction rate is much faster than the diffusion rate and diffusion is controlling.

II. The diffusion rate is much faster than the reaction rate on the catalyst surface and the surface reaction rate is controlling.

III. Neither rate is appreciably faster and neither is controlling.

CASE I. If the surface reaction rate is fast enough, the concentration of reactant at the catalyst surface (includes the space that extends about a mean free path above the actual surface) will be substantially equal to the equilibrium concentration, and the rate of disappearance of reactant from the fluid stream will be given by

$$-\frac{dy}{dt} = k_1(y - y^*) \tag{8}$$

where k_1 has the dimensions of reciprocal time and is a constant for a given system at a fixed temperature.

CASE II. If the diffusion rate is sufficiently fast relative to the rate of the surface reaction, the concentration of reactant on the catalyst surface will be substantially equal to the concentration in the gas stream, and, if the reaction is reversible and of apparent first order in both directions, the rate of disappearance of the reactant from the gas stream will be given by

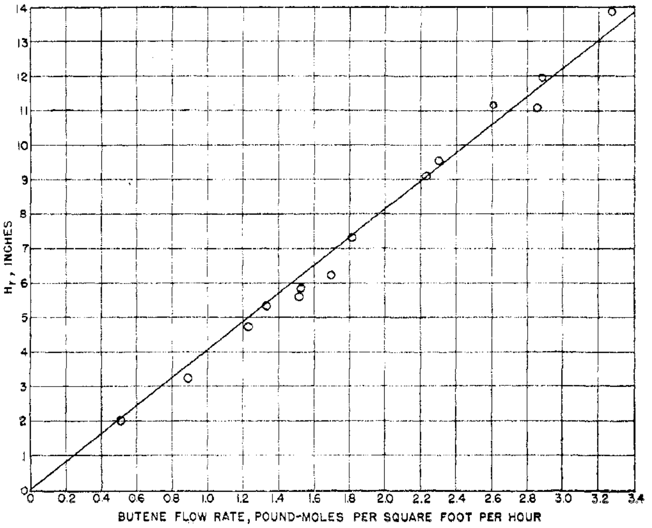

Figure 5. Effect of Higher Flow Rates on H_r at 350° C.

$$-\frac{dy}{dt} = k_2(y - y^*) \tag{9}$$

where k_2 is a constant having dimensions of reciprocal time and is a linear function of the specific reaction velocity constant.

For a reversible reaction of apparent first order in both directions in a reactor containing only the reactant and the primary product, if y is the mole fraction of reactant and k' and k'' the specific reaction velocity constants for the forward and reverse reactions, respectively, the rate of disappearance of reactant is given by

$$-\frac{dy}{dt} = k'y - k''(1 - y)$$

At equilibrium

$$-\frac{dy}{dt} = 0 \text{ and } k'' = \frac{k'y^*}{1 - y^*}$$

hence,

$$-\frac{dy}{dt} = \frac{k'(y - y^*)}{1 - y^*} \text{ and } k_2 = k'/(1 - y^*)$$

For the case of butene isomerization, it is here assumed that both *cis*- and *trans*-2-butene isomerize to 1-butene at the same rate.

CASE III. If y is the mole fraction of the reactant in the gas stream and y_i the corresponding mole fraction at the catalyst surface, the rate of disappearance of reactant from the fluid stream should be given by

$$-\frac{dy}{dt} = k_1(y - y_i) \tag{10}$$

If the surface reaction is reversible and apparent first order in both directions, the rate of appearance of product in the fluid stream at steady state will be equal to the rate of conversion on the catalyst surface and will be given by

$$\frac{d(1 - y)}{dt} = -\frac{dy_i}{dt} = k_2(y_i - y^*) \tag{11}$$

But since there is no accumulation on the surface,

$$\frac{d(1 - y)}{dt} = -\frac{dy}{dt} \tag{12}$$

so that

$$-\frac{dy}{dt} = k_1(y - y_i) = k_2(y_i - y^*) \tag{13}$$

Solving for y_i in Equation 13 and substituting in Equation 10,

$$-\frac{dy}{dt} = \frac{k_1k_2}{k_1 + k_2}(y - y^*) \tag{14}$$

Equation 14 is the general rate expression and is applicable to all three cases.

If the reaction had been assumed to involve three over-all steps such as diffusion, adsorption, and surface reaction, a third rate constant, k_3, would appear in Equation 14 which would then be written $-\frac{dy}{dt} = \frac{k_1k_2k_3}{k_1k_2 + k_2k_3 + k_1k_3}(y - y^*)$. Similarly, if four steps with four rate constants had been assumed, Equation 14 would become $-\frac{dy}{dt} = \frac{k_1k_2k_3k_4}{k_1k_2k_3 + k_1k_2k_4 + k_1k_3k_4 + k_2k_3k_4}(y - y^*)$. However, if case I applies and diffusion is controlling, k_2 will be large compared to k_1 so that k_1/k_2 will be small compared to unity and Equation 14 will reduce to Equation 8. Similarly, if case II applies, k_2/k_1 will be small compared to unity, and Equation 14 will reduce to Equation 9.

Combining Equations 6 and 14 gives

$$\frac{F}{\frac{k_1k_2}{k_1 + k_2}} = \frac{dZ}{\frac{-dy}{y - y^*}} \tag{15}$$

which is exactly equivalent to Equation 3 if H_r is defined by the expression

$$H_r = \frac{F}{\frac{k_1k_2}{k_1 + k_2}} \tag{16}$$

Substituting Equation 16 in Equation 15 and integrating,

$$H_r = \frac{Z}{\ln \frac{y_1 - y^*}{y_2 - y^*}} \tag{17}$$

which is the integrated form of Equation 3.

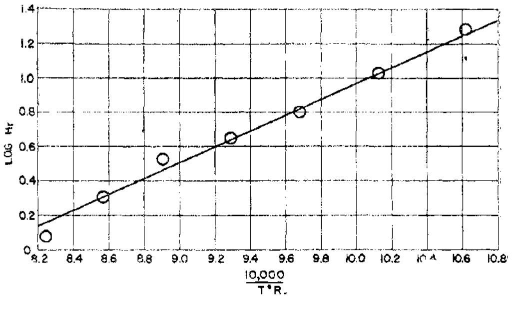

Figure 6. Relation between H_r and Temperature at Constant Apparent Gas Flow Rate of 480 Feet per Hour

Equation 16 indicates that H_r is directly proportional to the superficial linear fluid velocity in the reactor.

H_r for any experiment is obtained for a given set of conditions including a fixed flow rate. Also, Equations 15, 16, and 17 were derived assuming a fixed flow rate. However, for each flow rate, there will be a fixed value of H_r which should vary with flow rate according to Equation 16. This implies that k_1 and k_2 do not vary with flow rate. k_2 would be expected to be independent of flow rate; k_1, however, will be independent of flow rate only in the region of streamline flow. In all of the experiments reported in this paper other than those shown in Figure 5, the modified Reynolds number is less than 30 so that the flow is laminar. For turbulent flow, k_1 may vary appreciably with changing flow rate, though, if part of the diffusion process covered by the constant k_1 is diffusion down pores, k_1 will be less influenced

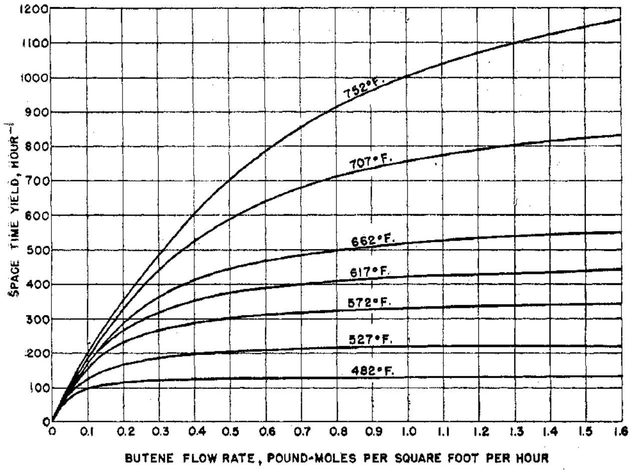

Figure 7. Variation of Space Time Yield with Flow Rate at Various Temperatures

by flow velocity than if the rate-controlling diffusion were entirely in the space between particles.

This relation can be used along with Equation 17 to predict the conversion for a specified set of conditions, when data are obtained under a different set of conditions. By use of Equation 17, H_r can be determined experimentally at high and low flow rates; these points in a plot of H_r versus flow rate can be joined by a straight line, and H_r at any intermediate flow rate can be taken from this plot. Then by again using Equation 17, with any two of the variables Z, y_1, or y_2 preselected, the third can be computed for this new flow rate.

At 662° F. a series of runs were made in which the flow rate range was extended to 3.27 lb.-moles/(sq. ft.) (hr.) and to a space velocity at 7100 hour^{-1}. These results, shown in Figure 5, indicate the linear relation between H_r and that the flow rate covers a wide range of flow rates. In this series the H_r values were not corrected for the changed catalyst activity.

EFFECT OF VARYING REACTION CONDITIONS

The effect of pressure is not predicted by these equations. However, for a given mass velocity, the linear velocity and, consequently, H_r will be inversely proportional to the pressure. Therefore, disregarding other effects of pressure, increasing the pressure should increase the conversion at a given mass velocity if the fluid is a gas.

The effect of temperature on H_r depends on whether the surface reaction or diffusion is controlling. Since H_r is equal to the linear flow rate divided by a constant, if diffusion through the bulk of the gas phase is controlling, this constant will be a direct function of the diffusion coefficient which varies approximately as $T^{3/2}$ (*9*). For this case the temperature dependence of H_r will be given by

$$H_r = \frac{F}{k_1} = \frac{F}{C_1 T^{3/2}} \qquad (18)$$

If the surface reaction is controlling, the constant will be a function of the reaction velocity constant

$$k_2 = \frac{k'}{1 - y^*} \qquad (19)$$

which is in turn related to temperature by the Arrhenius equation

$$k' = Ae^{-\Delta E/RT} \qquad (20$$

Since the surface reaction is controlling, k_1 is large compared to k_2 and Equation 16 will reduce to the form

$$H_r = \frac{F}{k_2} \qquad (21)$$

Combining Equations 19, 20, and 21 gives the temperature dependence of H_r,

$$H_r = \frac{F}{A}(1 - y^*)e^{\Delta E/RT} \qquad (22)$$

from which it is apparent that

$$\ln H_r = \ln \frac{F}{A}(1 - y^*) + \frac{\Delta E}{RT}$$

Hence, if the surface reaction is controlling, log H_r is shown to be approximately a linear function of $1/T$, complicated somewhat by a secondary dependence of ΔE and y^* on the temperature. Usually ΔE is assumed constant over comparatively short temperature intervals; for the isomerization of 1-butene to 2-butene, the value of $1-y^*$ will change by less than 3% over a temperature interval of 100° F.

In Figure 6 it is shown that at a constant gas velocity log H_r is roughly a linear function of $1/T$. The slope of the log H_r versus $1/T$ plot might be expected to be affected by any large correction for a change in the catalyst activity at 572° F. However, the points at the three lowest and the highest temperatures shown in Figure 6 involve corrections of not more than 10%. Therefore, the slope is not appreciably affected by the larger corrections used in obtaining the other points. Where this linear relation exists, it should be possible to make calculations for the design of a reactor to be used at one temperature when data obtained at some other temperature are available.

The effect of the catalyst pellet size can be estimated by data presented by Hurt (*8*). Other variables such as channeling and uncontrolled temperature variation in a larger reactor will adversely affect any correlation and must be corrected for by an empirical approach based on experience with a given reaction system.

SURFACE REACTION CONTROLLING

The fact that for these experiments log H_r versus $1/T$ is a straight line while a plot of H_r versus $T^{-3/2}$ is not indicates that the surface reaction and not diffusion of the reactant to the catalyst is controlling. The relative effects of the reaction and diffusion rates can be evaluated in another way. Hurt (*8*) gives a plot of H_t/(Schmidt number)$^{2/3}$ versus Reynolds number, for various sizes of packing. In the temperature range 482° to 752° F. for mixtures of 1- and 2-butene, (Schmidt number)$^{2/3}$ varies from 0.92 to 0.98. Under the experimental conditions the Reynolds number was in the range of 10 to 50. Using these values and Hurt's curve for 8- to 10-mesh particles, it is computed that H_t for these experiments varies from 0.19 to 0.31 inch. Because under these conditions H_r is found to vary from 1 to 14 inches, the reaction rate is shown to be considerably slower than the rate of mass transfer.

SPACE-TIME YIELD

The flow rates used in these experiments were low compared to those used in many mass transfer processes and some relatively fast catalytic reactions, but at each temperature, runs were made at flow rates above the optimum flow rate for the depth of catalyst bed used. The results show that the reaction rate is nearly independent of flow rate above a certain critical value at each temperature. The space-time yield in volumes of 1-butene (STP) reacting per volume of catalyst per hour is obtained by multiplying the space velocity of 1-butene by the fractional conversion to 2-butene. (The space velocity can be obtained by multiplying the flow rate given in Table I by 359 and dividing by the catalyst bed depth, $^1/_6$ foot.) These values are plotted against the flow rate in Figure 7. It is readily seen that at each temperature the conversion rate at first increases rapidly with increasing flow rate, but soon levels off and increases so slowly that within the experimental error it appears to be independent of flow rate. Therefore, in the lower flow rate region, increasing the flow rate materially increases the yield per unit of equipment per day, but this increase is less at higher flow rates and must be balanced against increased cost of gas handling and separation of the desired product which becomes a smaller fraction of the effluent gas at the high rates of flow. In these experiments the flow rate range covered at each temperature extends beyond the point where a further increase in the flow rate will result in a profitable increase in the space-time yield.

In plotting these curves of Figure 7 the H_r versus flow rate plot serves a useful purpose. Since that is a linear plot, it is easy to draw the straight line through a good average of the experimental points. Then from the average value of H_r at any flow rate a corresponding value for the space-time yield can be computed and smooth curves result. Further, some other value for the depth of the catalyst bed can be selected and similar curves drawn, from which the optimum flow rate can be estimated for the new catalyst bed.

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Carbonation of Aqueous Suspensions Containing Magnesium Oxides or Hydroxides

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olutions of magnesium bicarbonate having metastable concentrations more than twice the equilibrium concentration may be consistently prepared by leaching magnesium hydroxide, magnesium oxide, and calcined magnesite or dolomite with carbon dioxide and water. Metastable solutions cannot be prepared from magnesium carbonate or in the presence of precipitated magnesium carbonate or when the leaching temperature is much in excess of 30° C. Formation of metastable solutions of maximum concentration requires that the solution be kept nearly saturated by carbon dioxide; the solids should not be added at a rate in excess of that at which an equivalent amount of carbon dioxide is absorbed. The magnesium goes into solution as magnesium hydroxide; the hydroxide ion reacts with dissolved carbon dioxide to give bicarbonate ion, thereby allowing dissolution of magnesium hydroxide to continue. The principal reaction involved in the breakdown of solutions of metastable concentration is that between bicarbonate and hydroxyl ions, a reaction that occurs in a very narrow zone at the solid-liquid interface.

DURING a study of carbonic acid leaching of magnesite and dolomite it was observed that, under certain conditions, a metastable solution of magnesium carbonate could be produced in which the concentration of magnesium was more than twice the equilibrium concentration. This observation led to an extensive investigation to determine the practicability of applying this phenomenon in leaching magnesia from magnesite and dolomite by an improved Pattison process (*2*). Because of the importance of control of the metastable solution to the success of the process, an independent study was made to clarify the mechanism by which the metastable solution was formed and to establish the essential conditions required for producing and maintaining such a solution.

METASTABLE SOLUTION OF MAGNESIA BICARBONATE

Magnesium oxide or magnesium hydroxide is readily dissolved by an aqueous solution of carbon dioxide; magnesium carbonate is also taken into solution but at a much slower rate. The solid phase with which the solution is in equilibrium is not crystalline magnesium bicarbonate but may be either magnesium hydroxide or the hydrated carbonate, $MgCO_3.3H_2O$. The solubility of magnesium bicarbonate increases rapidly as the partial pressure of carbon dioxide is increased up to a pressure of 3.85×10^{-4} atmospheres or 0.28 mm. of mercury. Up to this point, the solid phase in equilibrium with the solution is magnesium hydroxide. As the partial pressure is increased further, the solubility of magnesium bicarbonate increases but at a slower rate, and the stable solid phase is magnesium carbonate trihydrate, known by the mineralogical name, nesquehonite. These solubility relations are shown in Figure 1, which was drawn from data obtained by Kline (*3*).

The metastable solubility of magnesium bicarbonate is repre-

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