

# Oxidation of Ethylene to Ethylene Oxide

## SHEN-WU WAN<sup>1</sup> Yale University, New Haven, Conn

THE vast potentialities of ethylene oxide as an organic intermediate in the chemical industry have stimulated many investigations dealing with the preparation, properties, and uses of this compound.

Of the two currently employed commercial processes for the manufacture of ethylene oxide, one is the two-step procedure, through ethylene chlorohydrin as the intermediate, while the other is the one-step direct oxidation of ethylene by air using a silver catalyst. However, with very few exceptions the latter process has been described only by patent literature which again has been limited mainly to reporting improvements on catalysts or anticatalysts. McClellan ( $\beta$ ) has pointed out the lack of published information on the design of plants using the latter process and the lack of published experimental data on this type of preparation aside from those of McBee, Hass, and Wiseman ( $\delta$ ). Since then, additional experimental data of the same type have been published (7, 9). A study of the reaction mechanism of ethylene oxidation was made by Twigg (10) under conditions different from industrial operation.

Although Messing (8) has indicated that the use of oxygen rather than air in the oxidation of ethylene to ethylene oxide has been investigated, no systematic experimental data have yet appeared in scientific journals to the best of the author's knowledge. Both the work of Murray (9) and that of McKim and Cambron (7) may be considered as a repetition and extension of that of McBee, Hass, and Wiseman. Their catalyst preparations differed somewhat in details but their main interests were all limited to air oxidation. Murray made a single experiment using an ethylene-oxygen mixture containing 4.77% ethylene, at an average temperature of  $249^{\circ}$  C., giving a 60.5% yield of ethylene oxide. Conversion and space velocity data were not perimental results for the catalytic oxidation of ethylene with oxygen over a wide range of feed composition as well as the results obtained for establishing an empirical kinetic relation for this oxidation over a limited range of feed composition.

#### Procedure

Except for difference in the material of construction and for certain safety measures against fire and explosion, the equipment used in this investigation and its operation were essentially the same as those adopted for another investigation on the catalytic oxidation of 4-carbon hydrocarbons, already described in detail (1); therefore, only the modifications need be described here. The reactor was constructed from a 3/8-inch outside diameter by  $\frac{5}{10}$ -inch inside diameter stainless steel tube bent into U shape. One arm of the U-tube served as the catalyst bed while the other arm was packed with 1/15-inch outside diameter glass Raschig rings to serve as a preheater. All connections were made with  $1/_4$ -inch outside diameter stainless steel tubing and stainless steel fittings and valves. Preliminary tests comparing the catalytic oxidation of ethylene with air in stainless steel and borosilicate glass reactors under otherwise identical conditions gave similar results, indicating no appreciable catalytic effect due to stainless steel. Other preliminary tests proved that the catalyst bed temperature, at all points, approached within 1° or 2° C. (except in run-away reactions) of that of the molten salt bath in which the reactor was immersed and of which the temperature was controlled to within  $\pm 0.2^{\circ}$  C. of the desired value.

In the first series of experiments which were of the nature of a general survey on the catalytic oxidation of ethylene with oxygen, the feed composition and the flow rate were adjusted directly through the reactor to within  $\pm 2\%$  of the values desired

reported. McKim and Cambron reported on two experiments using ethyleneoxygen feeds containing 91.0 and 95.7% ethylene, respectively, at 300° C. and a space velocity of 1800, the conversions to ethylene oxide being 3.8 and 1.8%, respectively, and the yields being 33.5 and 25.0%, respectively.

The author while working on a general project on the catalytic oxidation of hydrocarbons has accumulated considerable data on ethylene oxidation. The purpose of the present paper is to release the ex-<sup>1</sup> Present address, Chemical Construction Corp., New York, N.Y.



#### Table I. Catalytic Oxidation of Ethylene with Oxygen

**.**..

Run	Temp ° C	Space	Product concn., mole % (dry basis)	Conversion,	Yield,	Space-time	
1,0,	Feed Composition, Mole %, $90\%$ C <sub>2</sub> H <sub>4</sub> , $10\%$ O <sub>2</sub>						
1 2 3 4 5 6 7 8 9 10	210 230 230 240 240 240 250 250 260	3600 3600 1200 3600 1800 1200 3600 1800 3600	$\begin{array}{c} 0.82 \\ 1.51 \\ 2.20 \\ 2.60 \\ 2.21 \\ 3.10 \\ 3.65 \\ 2.86 \\ 3.75 \\ 3.85 \end{array}$	0.9 1.6 2.4 2.8 2.8 3.8 3.8 3.0 3.9 4.0	$\begin{array}{c} 68.5\\ 65.6\\ 64.8\\ 63.2\\ 64.0\\ 61.2\\ 60.3\\ 62.7\\ 59.1\\ 58.1 \end{array}$	$16.5 \\ 28.8 \\ 21.1 \\ 16.2 \\ 40.8 \\ 28.2 \\ 21.9 \\ 51.1 \\ 31.6 \\ 66.0 \\$	
		Feed Com	position, Mole %, 70%	C₂H₄, 30%	O2		
11 12 13 14 15 16 17 18 19 20 21 22 23 24	220 230 230 240 240 250 250 250 250 260 260 260 260 265	3600 3600 1200 3600 1800 1200 3600 1800 1200 3600 1800 1200 1800	$\begin{array}{c} 3.20\\ 4.84\\ 5.71\\ 6.53\\ 6.00\\ 6.92\\ 9.56\\ 5.95\\ 8.10\\ 9.42\\ 6.16\\ 8.25\\ 10.8\\ 10.3\\$	$\begin{array}{c} 4.1\\ 6.3\\ 6.9\\ 7.8\\ 7.6\\ 8.2\\ 10.8\\ 7.1\\ 9.3\\ 11.5\\ 8.4\\ 9.4\\ 12.5\\ 10.2\\ 10.$	64.4 62.8 61.3 61.2 57.5 58.6 57.7 56.4 56.0 57.3 57.3 56.8	$\begin{array}{c} 57.2\\ 86.0\\ 47.2\\ 35.6\\ 102.0\\ 48.3\\ 93.4\\ 61.3\\ 50.4\\ 110.0\\ 60.6\\ 53.8\\ 65.8 \end{array}$	
25	230	Feed Con 3600	position, Mole %, 50%	6 C <sub>2</sub> H <sub>4</sub> , 50%	O₂ 64 4	149 8	
26 27 28 29 30 31 32 33 34 35 36	$\begin{array}{c} 230\\ 230\\ 240\\ 240\\ 250\\ 250\\ 260\\ 260\\ 260\\ 260\\ 260\\ 260\\ \end{array}$	1800     1200     3600     1800     1200     3600     1800     1200     3600     1800     1200     3600     1800     1200	$12.9 \\ 14.6 \\ 11.2 \\ 12.6 \\ 13.4 \\ 12.7 \\ 13.4 \\ 12.7 \\ 14.8 \\ 15.7 \\ 16.9 \\ 17.7 \\ 17.7 \\ 17.7 \\ 14.8 \\ 15.7 \\ 16.9 \\ 17.7 \\ 17.7 \\ 16.9 \\ 17.7 \\ 17.7 \\ 17.7 \\ 10.0 \\ $	21.2 23.2 28.7 20.3 21.2 21.9 24.8 24.7 26.5	$\begin{array}{c} 63.1\\ 61.1\\ 61.3\\ 58.6\\ 57.4\\ 63.0\\ 58.8\\ 57.3\\ 61.1\\ 58.4\\ 57.2 \end{array}$	$\begin{array}{c} 103.7\\ 75.4\\ 179.0\\ 97.4\\ 67.6\\ 196.8\\ 103.4\\ 77.8\\ 226.9\\ 113.7\\ 81.4 \end{array}$	
		Feed Com	position, Mole %, 40%	C <sub>2</sub> H <sub>4</sub> , 60%	O2		
37 38 39 41 42 43 445 447 48 9 51	230 230 240 240 250 250 250 260 260 260 270 270 270	3600 1800 1200 3600 1800 1200 3600 1800 1200 3600 1800 1200 1800	1 10 3.80 8.20 8.42 8.30 12.8 12.0 13.5 15.5 13.9 17.7 21.8 15.6 23.4 24.5	$\begin{array}{c} 2.6\\ 8.7\\ 17.8\\ 19.2\\ 17.6\\ 26.3\\ 28.9\\ 31.7\\ 28.2\\ 35.2\\ 41.2\\ 35.2\\ 41.8\\ 44.8\\ \end{array}$	65.63 49.665.34 65.362.22 73.5168.52 67.0569.99 666.9	146.038.758.1146.367.167.1207.7108.679.3215.1180.1101.4229.3147.8105.6	
70 71 72 74 75 76 77 78 80 81 82 88 82 88 83 84	$\begin{array}{c} 215\\ 215\\ 225\\ 230\\ 230\\ 240\\ 240\\ 240\\ 240\\ 250\\ 250\\ 250\\ 260\\ 260\\ 260\\ 260\\ 260\end{array}$	Feed Com 8600 1800 3600 1800 1800 1200 3600 1200 3600 1200 3600 1200 1800 1200 1800 1200	position, Mole %, 30% 2.98 3.84 4.10 4.44 5.35 6.18 5.96 8.01 11.4 7.81 12.4 15.1 10.1 12.6 16.0	$\begin{array}{c} 9.7\\ 9.7\\ 12.1\\ 13.0\\ 14.0\\ 16.7\\ 18.9\\ 17.3\\ 24.0\\ 32.7\\ 23.2\\ 39.0\\ 28.8\\ 34.2\\ 41.4 \end{array}$	$\begin{array}{c} O_2 \\ 75.4 \\ 71.2 \\ 72.8 \\ 71.9 \\ 69.4 \\ 69.4 \\ 69.5 \\ 71.8 \\ 68.2 \\ 66.1 \\ 64.4 \\ 62.4 \\ 60.1 \\ 60.7 \end{array}$	$\begin{array}{c} 58.2\\ 36.9\\ 77.8\\ 81.9\\ 48.9\\ 99.0\\ 69.2\\ 62.3\\ 131.0\\ 96.6\\ 81.4\\ 159.8\\ 94.8\\ 76.3 \end{array}$	
85	230	Feed Com	position, Mole %, 20%	C <sub>2</sub> H <sub>4</sub> , 80%	O2	501	
866 887 889 9912 993 995 995 997 999 999	230 230 240 240 250 250 250 260 260 260 270 270 270 270	1800 1200 3600 1200 1800 1200 1800 1200 1800 1200 1800 18	5.55 4.37 4.42 6.06 7.82 5.42 7.50 9.62 7.55 8.85 10.4 7.33 8.38 9.40	16.9 18.8 18.0 25.2 32.3 22.5 31.3 39.5 31.5 36.6 41.8 36.6 41.8 47.5	75.0 74.1 75.2 74.12 74.7 71.1 72.6 70.5 72.6 71.2 67.2 67.2 67.1 665.1	$\begin{array}{c} 50.1 \\ 53.1 \\ 24.4 \\ 60.2 \\ 48.4 \\ 41.5 \\ 54.6 \\ 58.5 \\ 49.6 \\ 57.6 \\ 57.7 \\ 129.7 \\ 75.4 \\ 57.3 \end{array}$	
100	220	reed_Com 3600	position, Mole %, 15% 2.30	C <sub>2</sub> H <sub>4</sub> , 85%	O2 72 0	44 0	
101 102 103 104 105	240 260 270 280 280	3600 3600 3600 3600 1200	3,20 6,40 6,82 7,61 10,80	20.3 37.0 40.1 43.6 56.8	66.8 65.9 62.8 55.6 58.0	$\begin{array}{r} 58.5\\ 102.9\\ 109.6\\ 116.5\\ 50.4 \end{array}$	

for each experiment. In the second series of experiments devoted to the study of kinetics, a dummy reactor was connected in parallel with the actual reactor. It was packed only with the carrier material for the catalyst and was used during the time when the feed had to be adjusted to the proper composition. In this way the feed composition was made to approach within  $\pm 0.5\%$  of the value desired for any given experiment before it was introduced into the actual reactor. More care was also exercised in regulating the flow rate of the feed to within  $\pm 1\%$  of the desired value.

Another reactor was also used solely for conditioning catalysts, so that every charge of catalyst in the experimental reactor in each experiment would have approximately the same history as every other charge.

For the first series of experiments the catalyst was prepared by dissolving 100 grams of chemically pure silver nitrate in 800 ml. of distilled water; adding a 10% sodium hydroxide solution slowly and with constant stirring, leaving only a trace of excess silver nitrate in solution; adding 20 ml. of 30% hydrogen peroxide, settling, and decanting; washing the precipitate first by decantation and then on a filter with water containing 4 ml. of 30% hydrogen peroxide per 100 ml. until the washings were free from silver ions; transferring the precipitate to a porcelain dish and adding to it 400 grams of 14- to 20-mesh tabular alumina which had been previously screened, washed in boiling distilled water, and dried at 115° C.; stirring the slurry while adding 14 grams of chemically pure barium peroxide; continuing the stirring vigorously while evaporating the slurry nearly to dryness on a water bath; drying in an oven at 115° C. for 20 hours; and screening off the fines. The catalyst was further treated with 10% ethylene and 90% ni trogen at 250° C. for 3 hours and at 270° C. for 8 hours. Final conditioning was given the catalyst with an air-ethylene feed of 15 to 1 ratio at 260° C. for 40 hours. The catalyst was changed after each set of experiments made for one feed composition.

For the second series of experiments a larger batch of catalyst was prepared in a similar way and aged to the same extent in separate lots which were thoroughly mixed together again after the conditioning treatment. This batch of catalyst had a bulk density of 1.34 grams per cubic centimeter and contained 57% voids. Results of tests on these catalysts with air-ethylene feeds in ratios of 12 to 1 to 14 to 1, at 275° C. and a space velocity of 1800 to 3600, were in the order of 45 to 55% in conversion to ethylene used in this investigation was U.S.P. grade of 99.6% purity.

In the first series of experiments the reactor was filled with a single charge of catalyst to a depth of 30.3 cm. while the feed rate was varied from experiment to experiment to give the desired space velocities. In the second series of experiments a fixed superficial linear velocity of 30.3 cm. per second was maintained for the feed at the reactor inlet for all experiments while the amount of catalyst was varied to give beds of the following lengths: 30.3, 15.2, 9.1, 6.1, and 3.0 cm.

Ethylene oxide was determined by a modified titration method according to Lubatti (4) which was described in a previous publication (1), while ethylene, oxygen, and carbon dioxide were determined by standard gas analysis. Water was estimated by stoichiometry: Normally, no other component was present. In the kinetic experiments carbon dioxide was also

determined by absorption in a standard alkali solution followed by titration against a standard acid solution, after precipitating the carbonate with barium chloride. Gas analysis was also used as a check.

#### **Results and Discussion**

The first series of experiments covered a wide range of feed composition—from 90% ethylene and 10% oxygen to 15% ethylene and 85% oxygen. Both temperature and space velocity were somewhat restricted partly by the size of the reactor and partly by tendency toward explosion beyond certain limits. Space velocity is defined as the volumetric flow rate per hour of feed gas (measured at 1 atmosphere pressure absolute and at the



temperature of the reactor) divided by the volume of the catalyst bed, assuming it to be empty. Explosion occurred when temperature was raised rapidly beyond  $280^{\circ}$  C. or when space velocity was higher than 7200, especially for feeds of intermediate composition. For a space velocity lower than 1200, the gas stream was too small to be controlled and measured precisely. After some exploratory tests it was decided to limit the operation between 200° and 270° C. in temperature and between 1200 and 3600 in space velocity.

The lower and upper limits of flammability of ethylene in air and in oxygen and those of ethylene oxide in air have been reviewed by Coward and Jones (2). The values average about 3 and 29% of ethylene in air, 2.9 and 79.9% of ethylene in oxygen, and 3 and 80% of ethylene oxide in air. Therefore, most of the reaction mixtures in this investigation were explosive mixtures. In the air oxidation of ethylene, the initial mixture would also be explosive—unless the air-to-ethylene ratio exceeds 32.3, which is a very unlikely condition for commercial operation. Explosion can occur either as a result of an unbalanced chain-branching reaction or of a heat accumulation. The condition of branchedchain explosion can be simply defined when the mechanism is known. In this case, the chain mechanism is not known quantitatively (3). However, under the experimental conditions in-

Table II.	Catalytic (	Oxidation	of	Ethylene	with	Air	at
		275°C.					

Air-ethylene ratio Space velocity Conversion to ethylene oxide, % Yield of ethylene oxide, % Conceof ethylene oxide in	$12 \\ 1800 \\ 49.2 \\ 55.3$	$\substack{\substack{12\\3600\\45.4\\56.5}}$	$\substack{\begin{array}{c} 14 \\ 1800 \\ 54.8 \\ 61.6 \end{array}}$	${ \begin{smallmatrix} 14 \\ 3600 \\ 50.8 \\ 64.5 \end{smallmatrix} }$
product, mole % (dry basis) Space-time yield	$\substack{4.13\\33.9}$	$\begin{array}{c} 3.77\\62.3\end{array}$	$\begin{array}{c} 3.89\\ 35.3\end{array}$	$\begin{array}{c} 3.57\\64.8\end{array}$

### Table III. Kinetic Data of Ethylene Oxidation

		,	
(Fee	d composition, mole	%, 85% C2H4,	, 15% O2)
Catalyst Bed Length, Cm.	Conversion of C2H4 to C2H4O, %	Yield of C2H4O, %	Rate of C2H4O Pro- duction, Gram Mole/Hr./Gram of Catalyst
	Catalyst Bed Temper	$ature = 230^{\circ}$	С.
$\begin{array}{c} 30.3\\ 15.2\\ 9.1\\ 6.1\\ 3.0\\ 0 \end{array}$	2.05 1.10 0.671 0.463 0.182	$     \begin{array}{r}       60.5 \\       60.5 \\       59.7 \\       64.8 \\       61.3 \\       \dots     \end{array} $	$\begin{array}{c} 0.00114\\ 0.00122\\ 0.00124\\ 0.00128\\ 0.00128\\ 0.00128\\ 0.00127^{\alpha}\end{array}$
	Catalyst Bed Temper	ature = $240^{\circ}$	C.
$30.3 \\ 15.2 \\ 9.1 \\ 6.1 \\ 3.0 \\ 0$	$\begin{array}{c} 2.91 \\ 1.60 \\ 0.972 \\ 0.674 \\ 0.337 \\ \ldots \end{array}$	59.5 58.4 60.4 61.3 59.5	0.00157 0.00173 0.00176 0.00183 0.00183 0.00183
	Catalyst Bed Temper	ature = $260^{\circ}$	С.
$\begin{array}{c} 30.3\\ 15.2\\ 9.1\\ 6.1\\ 3.0\\ 0 \end{array}$	$5.41 \\ 3.14 \\ 2.01 \\ 1.41 \\ 0.699 \\ \dots$	58.7 59.6 60.5 59.7 60.4 	$\begin{array}{c} 0.00281 \\ 0.00322 \\ 0.00347 \\ 0.00366 \\ 0.00365 \\ 0.00386^a \end{array}$
<sup>a</sup> Extrapolated	values: $u_o = 30.3$ $\rho = 1.34$ ;	cm./sec. grams/sq. cm.	

volved, chain reactions are not expected to play any important part. The limit for thermal explosion is defined by the condition that the rate of accumulation of heat in the reaction vessel is zero—i.e., the rate of heat input due to reaction is just balanced by the rate of heat dissipation to surroundings. Quantitatively, this condition cannot be determined without a full knowledge of the kinetics of the reaction and the rates of heat transfer together with the thermal properties of the systems involved. Although kinetics have been made part of the object of this study, the measurement of heat transfer to produce data of design value is beyond the scope of the present investigation. Hence the region



of nonexplosive reaction was established qualitatively by the above-mentioned preliminary tests for the sake of this investigation.

Results are presented in Table I and Figures 1 and 2. The per cent conversion is defined as the per cent of ethylene in the feed converted to ethylene oxide; the per cent yield is defined as the per cent reacted ethylene which has become ethylene oxide; and the space-time-yield is defined as the volume of ethylene oxide as a hypothetical gas at standard temperature and pressure produced per hour per volume of catalyst bed, assuming it to be empty. By referring to Table I the following trends can be noted definitely:

1. For a given feed composition the conversion to ethylene oxide increases with temperature and decreases with space velocity.

2. For a given feed composition the per cent yield of ethylene oxide increases with space velocity but decreases with temperature.

3. Within the range studied, the space-time-yield always increases both with temperature and with space velocity.

4. At constant temperature and space velocity, the conversion first increases with the oxygen concentration of feed and then tends to become constant for oxygen concentrations above 70%.

5. At constant temperature and space velocity, the spacetime-yield first increases rapidly with the oxygen concentration, passes through a maximum, and then rapidly decreases with further increase in oxygen concentration in the feed.



Table V. Kinetic Data of Ethylene Oxidation

(Feed composition, mole%, $75\%$ C <sub>2</sub> H <sub>4</sub> , $25\%$ O <sub>2</sub> )							
Catalyst Bed Length, Cm.	Conversion of C <sub>2</sub> H <sub>4</sub> to C <sub>2</sub> H <sub>4</sub> O, %	Yield of C2H4O, %	Rate of C2H4O Production, Gram Mole/Hr./Gram_of Catalyst				
	Catalyst Bed Temp	erature = 230	° C.				
$30.3 \\ 15.2 \\ 9.1 \\ 6.1 \\ 3.0 \\ 0$	$\begin{array}{c} 3.10 \\ 1.68 \\ 1.02 \\ 0.683 \\ 0.348 \\ \cdots \end{array}$	$\begin{array}{c} 61.3\\ 60.2\\ 62.7\\ 61.2\\ 64.4\\ \end{array}$	$\begin{array}{c} 0.00152\\ 0.00164\\ 0.00166\\ 0.00168\\ 0.00168\\ 0.00169\\ 0.00171^a\end{array}$				
Catalyst Bed Temperature = $240^{\circ}$ C.							
$30.3 \\ 15.2 \\ 9.1 \\ 6.1 \\ 3.0 \\ 0$	4.42 2.41 1.49 1.03 0.524	58.7 57.5 59.5 62.4 61.2	$\begin{array}{c} 0.00219\\ 0.00229\\ 0.00240\\ 0.00247\\ 0.00247\\ 0.00247\\ 0.00247\\ 0.00249^a\end{array}$				
Catalyst Bed Temperature = $260^{\circ}$ C.							
30.3 15.2 9.1 6.1 3.0 0 • Extrapolated	7.79 4.81 3.10 2.16 1.12  values: $u_0 = 30.3$ cr	57.3 58.3 62.1 59.9 60.5 	$\begin{array}{c} 0.00357\\ 0.00440\\ 0.00475\\ 0.00496\\ 0.00503\\ 0.00518^{a}\end{array}$				
	$\rho = 1.34 \text{ gra}$	ams/cu. cm.					

6. The yield also varies with feed composition at constant temperature and space velocity and appears to be highest in the region of 30 to 40% ethylene. The trends described in items 4 and 5 are also illustrated in Figures 1 and 2. However, the trend described in item 6 does not lend itself to graphical representation on account of inconsistencies in the region of 30 to 40% ethylene in the feed. During three of the runs made in this region, for at least part of the duration of the experiment, gas analysis showed the absence of carbon dioxide while the absorbing solution for ethylene oxide recovery indicated the presence of peroxide. Attempts to reproduce the phenomena were not successful. Since the cause of these particular results has not been ascertained, they are considered erratic and hence omitted from the tables presented in this paper. One explosion also occurred in this region, but there was insufficient information to establish the exact cause.



For purpose of comparison, four typical results on the air oxidation of ethylene, while using the same catalyst, were presented in Table II. As compared with oxidation by air, the use of oxygen has, on the whole, the advantage of being able to give much higher space-time-yields—approximately four times—and much higher ethylene oxide concentrations in the product—approximately six times, within the range of conditions explored.

The second series of experiments yielded the data listed in Tables III to V. They were used for evaluating the constants for the following empirical kinetic equation:

$$\frac{dn}{d\theta} = k p^{a}_{C_2 H_4} p^{b}_{C_2} \tag{1}$$

where *n* equals gram moles of ethylene oxide produced per gram of catalyst;  $\theta$  equals time in hours; *p* is the partial pressure in atmospheres; and *a*, *b*, and *k* are empirical constants. The integral rates of ethylene oxide production in gram moles per hour per gram of catalyst were determined experimentally for different bed lengths for each given temperature and feed composition. They were plotted against bed length and the graph was extrapolated to zero bed length to determine  $\frac{dn}{d\theta}$  for the given set of conditions. The extrapolation is dependable because all the curves straighten out as they approach the axis and there is little scattering of data points. A set of three such values corresponding to three feed compositions at a given temperature was used to solve k, a, and b of Equation 1 for that temperature. Of the three sets of data available, that at 230° C. is not satisfactory for such computation because the rate values, being relatively



small, would require one more significant figure than those which were experimentally available in order to give numerical solutions of the same precision as those resulting from the other sets of data at 240° C. and 260° C. These latter data gave values of 0.365 and 0.316 for a: 0.667 and 0.677 for b: and 0.00708 and 0.0141 for k, at 240° C. and 260° C., respectively. From these, an average a and an average b were used together with the data at 230° C. to calculate k at 230° C., leading to the value of 0.00472. A semilogarithmic plot of k vs, the reciprocal of absolute temperature is remarkably linear (Figure 3) and leads to an activation energy value of 19,300 calories per gram mole.

Assuming gas ideality, constancy of a and b, and a constant average of 60% in ethylene oxide yield, Equation 1 can be graphically integrated to give the relation between catalyst bed length and the extent of reaction. The form of the equation to be integrated is as follows, when the total operating pressure is 1 atmosphere absolute:

$$dL = \frac{3600 \ S \ u_0 \left(1 - \frac{Sx}{2}\right)^a \left(1 - \frac{Sx}{2}\right)^b dx}{RTk \ \rho \left[S\left(1 - \frac{5x}{3}\right)\right]^a \left[1 - S - \frac{5Sx}{2}\right]^b}$$
(2)

in which L is length of catalyst bed in centimeters;  $u_{\bullet}$ , superficial

linear velocity of feed in centimeters per second (on the basis of gas measured at 1 atmosphere absolute, and at the temperature of the reactor assuming the latter to be empty); S, the mole fraction of ethylene in feed;  $\rho$ , the bulk density of catalyst in grams per cubic centimeter; R, the universal gas constant; T, temperature of reactor in degrees Kelvin; and x, the fractional conversion of ethylene in the feed to ethylene oxide. In Figures 4, 5, and 6, the values computed from Equation 2 are plotted as solid lines while the experimental values in Tables III to V are plotted as points. The agreement between the two is good. The constants of the empirical equation are expected to vary with the catalysts or with large changes in feed composition. However, the technique involved appears to be satisfactory in establishing an empirical kinetic equation for this reaction as a means of catalyst evaluation or of preliminary designing. The experiments performed with a 30.3-cm. catalyst bed were not essential



and a total of 36 experiments for the shorter beds would have been sufficient to evaluate the three constants and the activation energy. By using weighing burets and pipets the precision in ethylene oxide and carbon dioxide analysis could be easily improved to give results in four significant figures.

#### Literature Cited

- Bretton, Wan, and Dodge, IND. ENG. CHEM., 44, 594 (1952).
   Coward and Jones, U. S. Bur. Mines. Bull. 503 (1952).
   Lewis and Von Elbe, "Combustion, Flames and Explosions of Gases," New York, Academic Press, 1951.
- Lubatti, O. F., J. Soc. Chem. Ind., 51, 361 T (1932). (4)
- (5) McBee, Hass, and Wiseman, IND. ENG. CHEM., 37, 432 (1945).
- McClellan, Ibid., 42, 2402 (1950). (6)
- McKim, and Cambron, Can. J. Research, 27, 813 (1949). (7)
- Messing, R. F., Chem. Inds., 67, No. 1, 41 (1950). (8)
- (9) Murray, Australian J. Sci., 3A, 433 (1950).
   (10) Twigg, Trans. Faraday Soc., 42, 284 (1946).

RECEIVED for review June 2, 1952. ACCEPTED September 8, 1952.