



## Catalytic Oxidation of Ethylene under Moderately High Pressures

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# Catalytic Oxidation of Ethylene under Moderately High Pressures

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## Abstract

Many investigations have been reported about the oxidation of ethylene under ordinary pressure, but investigations under higher pressures are few. The authors made measurements on the rates of air oxidation of ethylene on a promoted silver catalyst supported on  $\alpha$ -alumina under moderately high pressures and correlated them in terms of total pressure and reactant concentrations.

## 1. Introduction

In the previous works<sup>1)</sup> the authors attempted to produce ethylene oxide efficiently by the catalytic oxidation of ethylene, and made clear the effects of various promoters and carriers to the activity and selectivity of the silver catalyst. Using the silver catalyst, promoted by potassium sulfate and supported on  $\alpha$ -alumina, the measurements were made on the rates of reaction between ethylene and oxygen to produce ethylene oxide, carbon dioxide and water. This data was analysed to formulate them into empirical kinetic equations<sup>2)</sup>.

In most gas-phase reactions, the operation at a higher pressure condition is more advantageous than at a lower pressure condition in that better space-time-yield would be obtained. Moreover, it is interesting from the kinetic aspect to know if the equations representing rate data under ordinary pressure will also fit those under higher pressures.

In spite of many reports that are seen about the catalytic oxidation of ethylene under ordinary pressure, there is few data about it under higher pressures. Hirasa and Hirayama<sup>3)</sup>, using their mixed catalyst composed of active silver and electrolytic silver, showed that the oxidation rate of ethylene to ethylene oxide is proportional to 0.30 power of total pressure, 0.22 power of oxygen concentration, and 2.26 power of ethylene concentration.

The purpose of this work is to measure the rate of air oxidation of ethylene on the promoted silver catalyst (supported on  $\alpha$ -alumina) under moderately high pressures and to find its dependence on total pressure and reactant concentrations.

## 2. Experimental

### 2-1. Catalyst Preparation

The catalyst was prepared according to the method described elsewhere<sup>2)</sup>.

50 grams of spherical catalyst was used on this experiment.

### 2-2. Preparation of Mixed Gas

Ethylene was supplied by Japan Petrochemical Co., air by Hokkai-Sanso Co. These gases were mixed in a cylinder. The mixed gas contained  $2.5 \pm 0.1$  per cent ethylene and was supplied through a regulating valve and a rotameter to the reacting system.

### 2-3. Apparatus

The reactor consisted of a 40-mm  $\phi$  stainless steel pipe 700 mm long, immersed completely in a salt bath ( $\text{KNO}_3\text{-NaNO}_3$ ). An alumel-chromel thermocouple was inserted through the center of the reactor tube. The catalyst bed support was located at 300 mm height from the bottom of the tube, about 20 mm height of 5 mm  $\phi$  alundum beads were put on the support and the catalyst was placed upon them.

Three pipe-heaters were used for heating the bath, one of them was connected to the temperature controller. Because considerable temperature difference through the catalyst bed was observed in the case of high pressure operation, the control heater was adjusted so that the average temperature through the catalyst bed would indicate the predetermined value.

The pressure and flow rate of inlet gas were closely controlled using fine regulating valves fitted at the inlet and outlet sides of the reactor.

The pressure drop across the bed was negligible between 0 and 15 kg/cm<sup>2</sup> (gauge) pressure range. Ethylene, ethylene oxide and carbon dioxide were analysed by means of gas chromatography. The column used for the separation of ethylene and carbon dioxide consisted of 80 cm of 4-mm  $\phi$  copper tubing containing 30-50 mesh active carbon. The column used for the separation of ethylene oxide consisted of 200 cm of 4-mm  $\phi$  copper tubing containing D. O. P. on 30-50 mesh cerite.

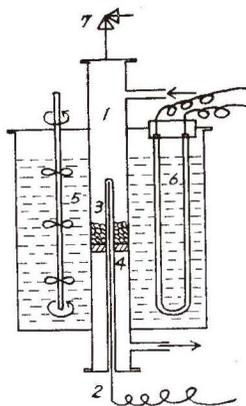


Fig. 1. Reactor

- 1: Reactor-tube, 2: Thermocouple,  
3: Catalyst, 4: Catalyst-bed support,  
5: Salt-bath, 6: Pipe-heater,  
7: Safety-valve.

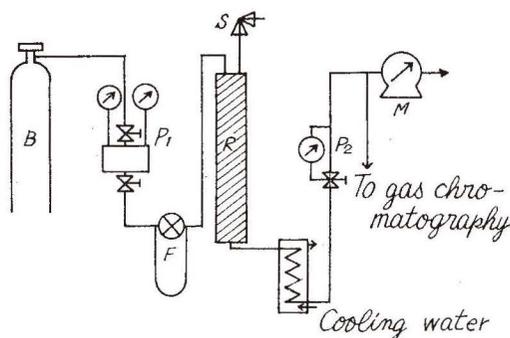


Fig. 2. Flow diagram

- B: Feedgas storage cylinder,  $P_1$ : Pressure and flow rate regulator, F: Rotameter, S: Safety-valve, R: Reactor,  $P_2$ : Pressure gauge, M: Gas-meter.

The temperature was 70°C, and the carrier gas (hydrogen) flow rates were 58 and 36 ml per min, respectively.

### 3. Results

#### 3-1. The Change of Catalyst Activity during Reaction Period

200°C of catalyst average temperature, 12.8 liters per hour of feed rate (N.T.P.), and 1 atm total pressure were chosen as the standard condition. At this condition the catalyst activity was tested frequently for 1600 hours [Fig. 3]. Each conversion ( $x$  and  $y$ ) is the average value of two experiments. It may be seen that about thirty hours are needed for approximate stabilization and that stable catalyst activity continues for a considerably long period.

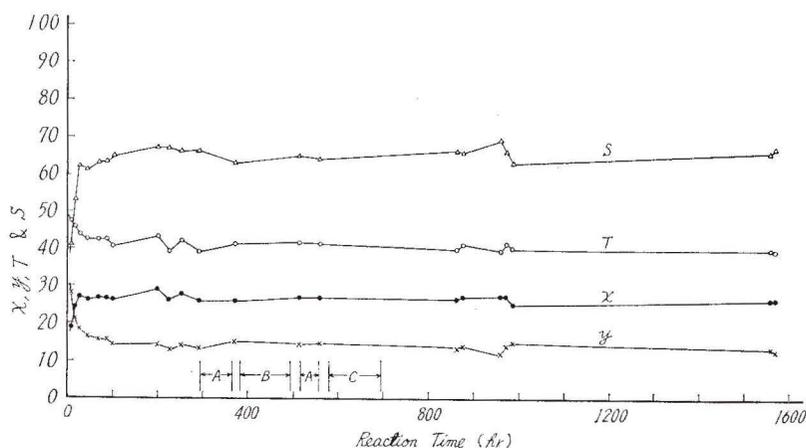


Fig. 3. Results of conditioning and check runs

( $T_m = 200^\circ\text{C}$ ,  $W = 50$  g,  $F = 1.43 \times 10^{-2}$  g-mole- $\text{C}_2\text{H}_4/\text{hr}$ ,  $P = 1.00$  atm)

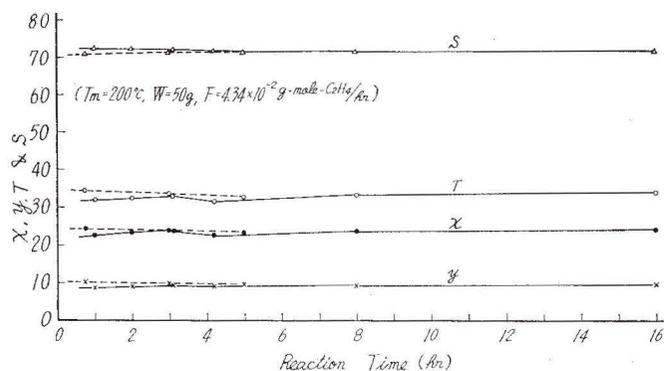


Fig. 4. Effect of changes of pressure level.

— The total pressure is changed from 1.00 atm to 5.84 atm.  
 ..... The total pressure is changed from 10.68 atm to 5.84 atm.

### 3-2. Unsteady Catalyst Activity due to Change of Operating Pressure

If the operating pressure is changed upwards at constant temperature and flow rate, the total conversion increases slowly. The reverse occurs when the pressure level is reduced. When the pressure level is altered, the constant conversions are realized within four or five hours. Some typical results are shown in Fig. 4. Moreover, it is known by the authors' previous work that if the temperature level or flow rate level is altered, the steady conversions are obtained within two or three hours. Considering these facts the conversion data corresponding to one set of reaction conditions were determined at about five hours after the reaction conditions reached the predetermined values.

### 3-3. Temperature Distribution along the Catalyst Bed

Because of the large heat of reaction, particularly due to the combustion of ethylene, longitudinal temperature gradient is observed especially in the case of high pressure conditions. Some typical longitudinal profiles at the center of the

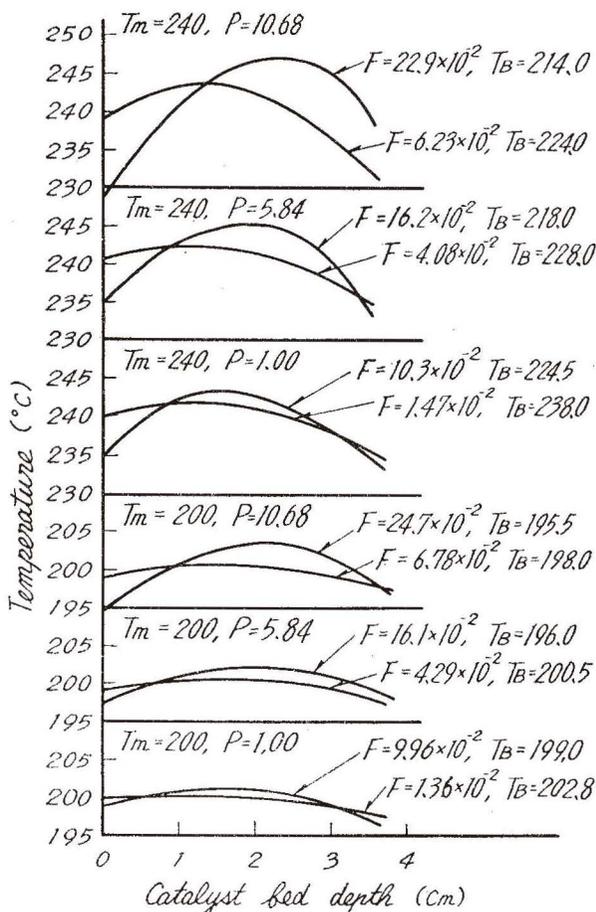


Fig. 5. Typical temperature distribution curves through catalyst bed.

bed are shown in Fig. 5. Therefore, the average temperature at the center of the catalyst bed was used as the reaction temperature.

### 3-4. Reaction Rates

Table 1 shows the results of kinetic runs, which were done during the time intervals indicated in Fig. 3 (A, B and C). During the period A the temperature level was fixed at 200°C and conversion measurements were performed at various pressures and reaction times ( $W/F$ ). During the period B and C, the temperature levels were kept at 240 and 265°C, respectively. Frequent checks for the standard condition indicated almost constant conversions within experimental error, and hence

Table 1. Reaction rate data

$T_m$	$P$	$W/F$	$x$	$y$	$a \times 10^2$	$b \times 10^2$	$c \times 10^2$	$d \times 10^2$	$r \times 10^4$	$v \times 10^4$
200	1.00	0	0	0	2.50	20.41	0	0	2.28	0.88
		100	2.05	0.80	2.43	20.33	0.051	0.040	1.89	0.80
		200	3.75	1.55	2.37	20.26	0.094	0.078	1.64	0.73
		400	6.70	2.85	2.26	20.13	0.168	0.143	1.29	0.62
		800	10.95	5.05	2.10	19.92	0.274	0.253	0.96	0.475
		1200	14.55	6.70	1.97	19.76	0.364	0.336	0.785	0.39
		1600	17.60	8.15	1.86	19.62	0.441	0.408	0.67	0.35
		2000	20.15	9.50	1.76	19.49	0.505	0.476	0.575	0.325
		2400	22.35	10.80	1.68	19.37	0.560	0.542	0.49	0.31
		2800	24.10	12.10	1.60	19.26	0.604	0.607	0.405	0.29
		3200	25.45	13.30	1.54	19.16	0.638	0.667	0.325	0.275
		3600	26.70	14.45	1.48	19.06	0.670	0.725	0.25	0.275
5.84	0	0	0	0	2.50	20.41	0	0	4.65	1.28
		100	3.60	1.20	2.38	20.28	0.090	0.060	3.03	1.13
		200	6.30	2.25	2.29	20.18	0.158	0.113	2.47	1.02
		400	10.60	4.15	2.13	19.99	0.265	0.208	1.93	0.87
		600	14.20	5.80	2.00	19.83	0.356	0.291	1.66	0.77
		800	17.20	7.30	1.89	19.69	0.431	0.366	1.48	0.705
		1000	20.10	8.60	1.79	19.56	0.504	0.431	1.375	0.66
		1200	22.90	9.90	1.68	19.44	0.574	0.496	1.30	0.625
1400	25.45	11.15	1.59	19.32	0.638	0.559	1.24	0.60		
10.68	0	0	0	0	2.50	20.41	0	0	6.40	1.82
		100	4.30	1.55	2.36	20.25	0.108	0.078	3.58	1.375
		200	7.60	2.75	2.24	20.13	0.190	0.138	2.78	1.18
		400	12.50	4.95	2.07	19.91	0.313	0.248	2.15	0.975
		600	16.50	6.80	1.92	19.73	0.413	0.341	1.93	0.86
		800	20.20	8.45	1.72	19.50	0.552	0.461	1.82	0.78
		1000	23.75	9.90	1.66	19.43	0.596	0.496	1.76	0.715

$T_m$	$P$	$W/F$	$x$	$y$	$a \times 10^2$	$b \times 10^2$	$c \times 10^2$	$d \times 10^2$	$r \times 10^4$	$v \times 10^4$	
240	1.00	0	0	0	2.50	20.41	0	0	5.52	4.90	
		100	5.20	3.75	2.28	20.08	0.130	0.188	4.86	3.31	
		200	9.65	6.40	2.10	19.83	0.242	0.320	4.23	2.64	
		400	17.15	10.70	1.81	19.44	0.430	0.536	3.23	1.93	
		800	27.50	17.20	1.39	18.84	0.690	0.863	2.06	1.40	
		1200	34.25	22.15	1.09	18.40	0.860	1.11	1.42	1.08	
		1600	39.10	26.15	0.873	18.05	0.982	1.31	0.99	0.89	
		2000	42.50	29.30	0.709	17.78	1.07	1.47	0.69	0.76	
		2400	44.80	32.05	0.582	17.55	1.13	1.61	0.47	0.67	
		2800	46.35	34.50	0.482	17.34	1.17	1.74	0.30	0.58	
	3200	47.15	36.85	0.402	17.16	1.19	1.85	0.16	0.50		
	3600	47.50	38.90	0.342	17.00	1.19	1.96	0.05	0.43		
	5.84	0	0	0	2.50	20.41	0	0	12.15	6.83	
		100	9.80	5.40	2.12	19.91	0.245	0.270	8.00	4.82	
		200	16.55	8.85	1.87	19.58	0.415	0.443	6.04	3.60	
		400	26.70	14.70	1.47	19.04	0.670	0.737	4.19	2.57	
		600	33.95	19.20	1.18	18.62	0.852	0.964	3.05	2.11	
		800	39.40	23.20	0.940	18.27	0.990	1.17	2.21	1.84	
		1000	43.20	26.65	0.758	17.97	1.09	1.34	1.58	1.64	
		1200	45.55	29.80	0.620	17.71	1.15	1.50	1.03	1.47	
	1400	47.00	32.60	0.513	17.48	1.18	1.64	0.55	1.34		
	10.68	0	0	0	2.50	20.41	0	0	14.18	8.50	
		100	11.60	5.75	2.07	19.86	0.290	0.288	9.88	4.49	
		200	20.05	9.60	1.76	19.49	0.503	0.481	7.12	3.58	
		400	31.30	16.00	1.32	18.89	0.786	0.803	4.28	2.81	
		600	37.95	21.15	1.03	18.44	0.953	1.06	2.48	2.36	
		800	41.80	25.60	0.819	18.06	1.05	1.29	1.51	2.10	
		1000	44.20	29.60	0.659	17.74	1.11	1.49	0.96	1.94	
	265	1.00	0	0	0	2.50	20.41	0	0	8.72	7.90
			100	8.00	7.00	2.13	19.80	0.200	0.350	7.63	6.00
200			15.25	12.30	1.81	19.33	0.382	0.616	6.57	4.60	
400			26.70	19.90	1.34	18.65	0.670	0.998	4.70	2.98	
800			39.00	28.30	0.822	17.89	0.980	1.42	2.04	1.62	
1200			44.20	33.50	0.561	17.44	1.11	1.68	0.80	1.10	
1600			45.75	37.35	0.425	17.13	1.15	1.88	0.22	0.83	
2000			45.65	40.50	0.348	16.90	1.15	2.04	-0.06	0.72	
2400			45.05	43.20	0.295	16.70	1.13	2.17	-0.18	0.65	
2800			44.35	45.70	0.250	16.52	1.11	2.30	-0.21	0.60	
3200			43.70	48.05	0.207	16.35	1.10	2.42	-0.22	0.56	
3600			42.75	50.30	0.175	16.19	1.07	2.53	-0.24	0.53	

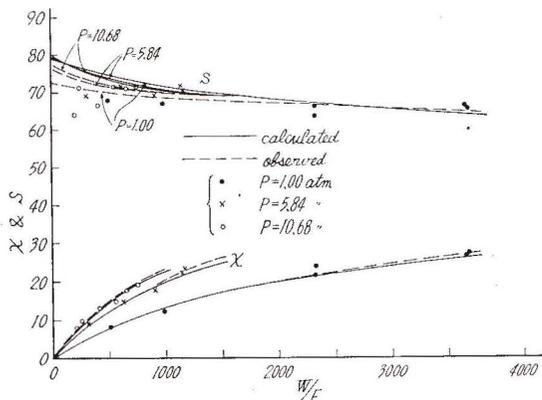


Fig. 6-1. Conversion of  $C_2H_4$  to  $C_2H_4O$  and selectivity at  $200^\circ C$  vs. reaction time for various total pressures.

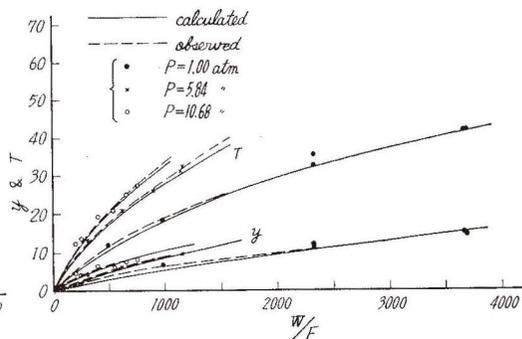


Fig. 6-2. Conversion of  $C_2H_4$  to  $CO_2$  and total conversion at  $200^\circ C$  vs. reaction time for various total pressures.

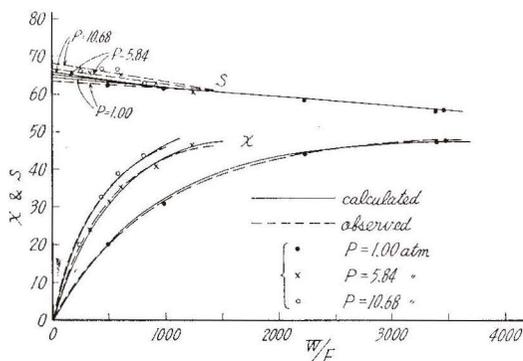


Fig. 7-1. Conversion of  $C_2H_4$  to  $C_2H_4O$  and selectivity at  $240^\circ C$  vs. reaction time for various total pressures.

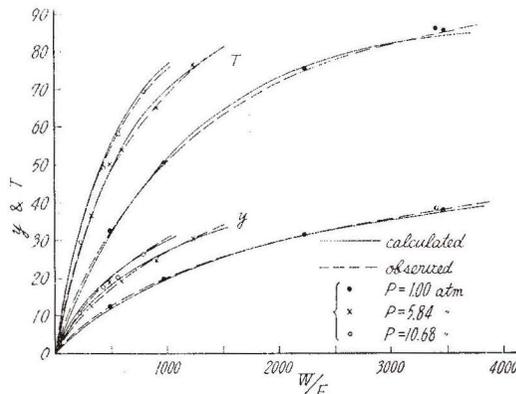


Fig. 7-2. Conversion of  $C_2H_4$  to  $CO_2$  and total conversion at  $240^\circ C$  vs. reaction time for various total pressures.

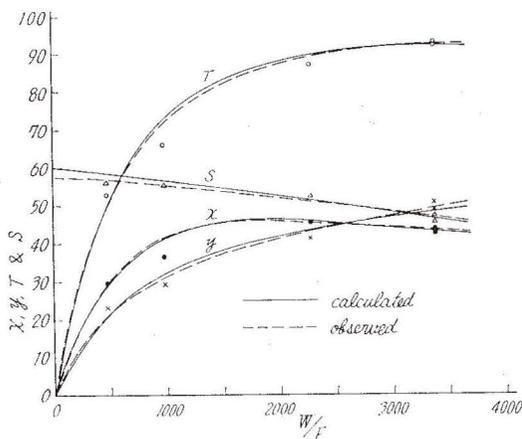


Fig. 8. Conversion of  $C_2H_4$  to  $C_2H_4O$ ,  $CO_2$ , total conversion and selectivity at  $265^\circ C$  vs. reaction time for 1 atm pressure.

the surface was assumed to be in the same reference state.

The rates of reaction ( $r$  and  $v$ ) were calculated at each reaction time from the plots of conversions to ethylene oxide and carbon dioxide versus reaction time coordinate (Fig. 6-1, 6-2, 7-1, 7-2 and 8). These are tabulated in Table 1. In Table 1 the corresponding mole fractions of gaseous constituents are also presented.

#### 4. Quantitative Evaluation of Rate Constants

In the previous paper<sup>2)</sup>, the authors have presented following rate equations by analysing their experimental data which was obtained by using the same type of catalyst as used in this work.

$$r = k_1 p_1 p_2^{\frac{1}{2}} - k_2 p_3 p_4^{-\frac{1}{2}}$$

$$v = k_3 p_1 p_2$$

The rate data under ordinary pressure presented in Table 1 fitted nicely to these rate equations as shown in Fig. 6-1, 6-2, 7-1, 7-2 and 8. Full lines in these figures represent calculated values using these equations.

If these equations were based on strictly correct mechanism, each rate constant would not vary with total pressure as long as the reaction temperature is kept at a constant level.  $k_1$ ,  $k_2$  and  $k_3$  were calculated by inserting the experimental data under the high pressure conditions into these equations, and it was found that these constants decrease as the total pressure increases (Table 2). Therefore it can not be possible to represent the data under different pressures by the same rate equations which are satisfactory under ordinary pressure.

Table 2. Rate constants

$T_m$	$P$	I			II			III
		$k_1 \times 10^2$	$k_2 \times 10^2$	$k_3 \times 10^2$	$(k_1)_P \times 10^2$	$(k_2)_P \times 10^2$	$(k_3)_P \times 10^2$	
200	1.00	1.970	0.1367	1.098	1.970	0.1367	1.098	} $l=0.33$ $m=0.24$ $n=0.32$
	5.84	0.2197	0.0583	0.0588	3.527	0.2088	1.931	
	10.68	0.1102	0.0562	0.0213	4.304	0.2413	2.343	
240	1.00	4.930	0.0904	5.880	4.930	0.0904	5.880	
	5.84	0.6281	0.0641	0.3173	8.825	0.1381	10.34	
	10.68	0.3530	0.0940	0.1052	10.77	0.1596	12.55	
265	1.00	8.759	0.1375	12.82	8.759	0.1375	12.82	

Now, assuming that each rate constant involves a function of total pressure  $P$ , the authors tried to represent their data with the following empirical equations:

$$r = (k_1)_P ab^{\frac{1}{2}} - (k_2)_P cd^{-\frac{1}{2}}$$

$$= (k_1)_1 P^l ab^{\frac{1}{2}} - (k_2)_1 P^m cd^{-\frac{1}{2}} \quad (1)$$

and

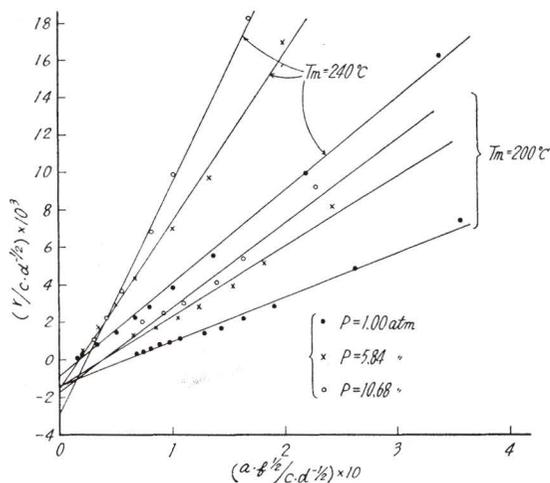


Fig. 9-1. Test of equation (3)

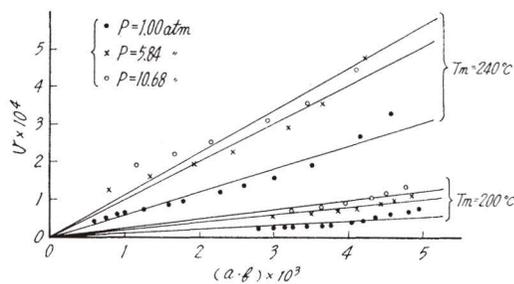


Fig. 9-2. Test of equation (2)

$$\begin{aligned} v &= (k_3)_P ab \\ &= (k_3)_1 P^n ab \end{aligned} \quad (2)$$

where  $(k_1)_P$ ,  $(k_2)_P$  and  $(k_3)_P$  are constant at a fixed temperature and pressure,  $(k_1)_1$ ,  $(k_2)_1$  and  $(k_3)_1$  are rate constants on 1 atm pressure, and  $a$ ,  $b$ ,  $c$  and  $d$  are mole fractions of ethylene, oxygen, ethylene oxide and carbon dioxide, respectively.

Rearranging equation (1), we obtain

$$r/cd^{-\frac{1}{2}} = (k_1)_P ab^{\frac{1}{2}}/cd^{-\frac{1}{2}} - (k_2)_P \quad (3)$$

The equations (3) and (2) in linear form appear to fit each set of data under each fixed total pressure as shown in Fig. 9-1 and 9-2. The constants,  $(k_1)_P$ ,  $(k_2)_P$  and  $(k_3)_P$  were evaluated by least squares and are tabulated in Table 2 at each experimental temperature and pressure.  $l$ ,  $m$  and  $n$  were determined from the following relations:

$$(k_1)_P = (k_1)_1 P^l \quad (4)$$

$$(k_2)_P = (k_2)_1 P^m \quad (5)$$

and

$$(k_3)_P = (k_3)_1 P^n \quad (6)$$

Numerical values of  $l$ ,  $m$  and  $n$  are also presented in Table 2.

## 5. Conclusions

An investigation of the silver-catalyzed reaction between ethylene and air under

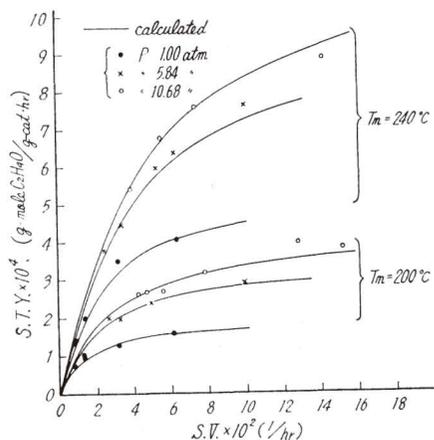


Fig. 10. Space-time-yield vs. space-velocity at different pressures and temperatures.

moderately high pressures is described. It was found that (1) as was expected, conversions both to ethylene oxide ( $x$ ) and carbon dioxide ( $y$ ) are larger as the pressure increases at a given  $W/F$ ; consequently, at a given S.V. the increase in pressure results in higher space-time-yield (S.T.Y.) as shown in Fig. 10; and that (2) the kinetic equations which fit the rate data under ordinary pressure can not be applied to the data under higher pressures satisfactorily. The reasons of this can not be answered at present. However, one may be ascribed to the fact that a definite value of temperature can not be assigned to one set of reaction, because temperature gradient across the catalyst bed becomes considerably large at high pressures and high flow rates. However, this may not be the primary reason, but rather it may be ascribed to the fact that the oxidation of ethylene is a complex reaction involving parallel and consecutive reactions, adsorbed states of reactants and products are not yet clearly understood, and consequently it is a rather difficult task to obtain the correct kinetic equations. In other words, it may be stated that the mechanism of the reaction would be made clear gradually by experiments under the wide range of operating pressures including the change of partial pressures of each reactant and product.

The authors could represent their kinetic data under both the ordinary and moderately high pressures by the empirical rate equations including total pressure terms in them.

The electronic computer FACOM 231 of the Muroran Institute of Technology served for the analyses of the reaction rate data.

### Acknowledgment

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### Nomenclature

$T_m$  = average catalyst bed temperature, °C.

$T_B$  = temperature of salt bath, °C.

$x$  = conversion of ethylene to ethylene oxide, %.

$y$  = conversion of ethylene to carbon dioxide and water, %.

$T$  = total conversion,  $x + y$ , %.

$S$  = selectivity,  $100 [x/(x+y)]$ , %.

$W$  = weight of catalyst used, g.

$F$  = feed rate, g-moles- $C_2H_4$ /hr.

$r$  = gram moles  $C_2H_4$  converted to  $C_2H_4O$  per unit time per unit mass of catalyst,  
g-moles- $C_2H_4$ /hr · g-catalyst

$v$  = gram moles  $C_2H_4$  converted to  $CO_2$  per unit time per unit mass of catalyst,

g-moles- $C_2H_4$ /hr · g-catalyst

$p_1, p_2, p_3, p_4$  = partial pressures of ethylene, oxygen, ethylene oxide and carbon dioxide, respectively, atm.

$a, b, c, d$  = mole fractions of ethylene, oxygen, ethylene oxide and carbon dioxide, respectively

$(k_1)_P, (k_2)_P, (k_3)_P$  = constants at fixed pressure  $P$

$(k_1)_1, (k_2)_1, (k_3)_1$  = constants at 1 atm pressure

$l, m, n$  = constants

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