T_m = absolute temperature of surface m (T)
ΔT_b = temperature drop across bed based on linear portion of distribution in bed (T)
ΔT_c = temperature discontinuity at heater surface (T)
ΔT_{ov} = over-all temperature drop across bed (T)
ΔT_w = temperature discontinuity at container wall (T)
W_m = radiant energy emitted by reference area S_m per unit time (units same as for I_m)

Greek Letters

α = average effective absorptivity of gray surface of layer of particles one average particle spacing thick (dimensionless)
α_m = effective absorptivity of gray surface m (dimensionless)
γ = ratio of heat transfer by radiation to heat transfer by conduction (dimensionless)
ρ = average effective reflectivity of gray surface of layer of particles one average particle spacing thick (dimensionless)
ρ_m = effective reflectivity of gray surface m (dimensionless)
ρ_w = reflectivity of an opaque bounding surface (dimensionless)
σ = Stefan-Boltzmann constant, 1.378×10^{-12} cal./(sec.)(sq. cm.)(°K.)^4
τ = average effective transmissivity of layer of particles one average particle spacing thick (dimensionless)

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The Vapor-phase Catalytic Hydration of Ethylene Oxide to Glycols

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The vapor-phase reaction between ethylene oxide and water to form glycols has been carried out under a wide range of conditions with particles of polystyrene–sulfonic acid ion exchange resins used as catalysts. The rates observed appeared to be directly proportional to the product of the partial pressure of ethylene oxide and the amount of water sorbed by the resin. By use of the Brunauer, Emmett, and Teller equation to describe the amount of water sorbed by the resin, the experimental data were correlated over a sixty-fold range of reaction rates with a mean deviation of 15%.

To obtain data of value in elucidating reaction mechanisms, the reactor was usually run under "differential" conditions, that is low conversions. However in a few runs conversions of as high as 54% were obtained for a contact time of 0.02 sec. The ratio of ethylene glycol to higher glycols (selectivity) obtained varied between 73 and 99% but was usually above 80% under conditions of high conversion. However it could also be reduced forcibly to produce higher glycols as the major product, if desired.

The growing demand for ethylene-glycol has stimulated a great deal of research. Until recently all the ethylene oxide hydration studies were concentrated on understanding the homogeneous reaction, primarily the sulfuric-acid catalyzed reaction (*2, 5, 11, 12, 14*) between water and dissolved ethylene oxide. Of the heterogeneous solid catalyzed reactions, the more interesting ones appear to be those involving a strong hydrogen ion exchange resin as the catalyst. Othmer and Thakar (*12*) studied the use of batch and fluidized beds for the liquid-solid heterogeneous system. Reed, Wenzel, and O'Hara (*15*) published data on a continuous packed-bed reactor for the vapor-solid and vapor-

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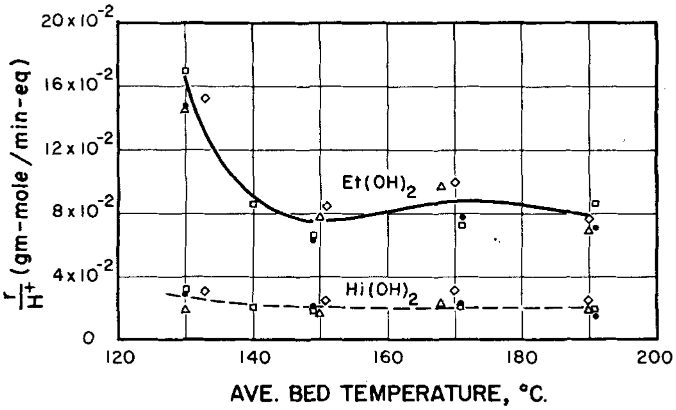

Fig. 1. Effects of Reynolds number and temperature on reaction rates.

Symbol	Molal ratio, water: EtO	Reynolds number
◇	10:1	200.
●	15:1	100.
△	10:1	150.
○	10:1	250.
□	10:1	50.

Pressure: 35.7 lb./sq. in abs.
Particle diameter: 0.78 mm. (air dried).

liquid-solid heterogeneous systems. The data obtained from the continuous fluidized and packed-bed reactors were of limited value in the understanding of the kinetics of the reactions, owing to the narrow ranges of conditions studied and to the fact that the reactors were of the integral type. At approximately the same time that Reed was carrying out studies on an integral reactor Hamilton and Metzner (*9*) were studying the vapor-solid reaction using a differential packed bed. These latter studies showed a pronounced effect of Reynolds number on reaction rates. The object of this work was to extend the ranges of these data to higher Reynolds numbers and to study pressure effects.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Details of equipment and procedure are described elsewhere (*6*). In general, the reactor as well as the operational and analytical procedures were all similar to those used by Hamilton (*9*) but with the following important improvements:

1. More accurate metering of both steam and ethylene oxide was achieved by replacing the gas-phase metering apparatus used previously. In this work the necessary steam was produced by pumping distilled water into a vaporizer with a metering pump, and flow rates of liquid ethylene oxide were measured with rotameters.
2. The ethylene oxide was vaporized in a steam-heated chamber packed with ball bearings just before it entered the reactor. This vaporizer served as an effective knock-out trap for polymers of ethylene oxide, thereby ensuring a clean vapor feed to the catalyst.
3. Physical analytical procedures (such as distillation or refractive-index measurements) used frequently by previous workers do not provide the degree of accuracy desired; therefore, chemical methods were used exclusively. For determination of ethylene glycol and of unreacted ethylene oxide in the product samples periodic acid oxidation and the Lubatti (magnesium chloride-hydrochloric acid) method respectively were used as before (*9*). For determination of the presence of higher glycols, Hamilton and Metzner used a dichromate oxidation which effectively determined all higher glycols as well as any ethylene oxide polymers. Conclusively to avoid errors due to the presence of the latter in this work the higher glycols were determined by colorimetric analysis, with colored complexes which may be formed between the hydroxyl groups on the glycols and ammonium hexanitratocerate (*4*). For this purpose a Beckman colorimeter, operated at a wave length of 542 mμ., was used.

All analytical procedures were thoroughly tested with mixtures of known composition as well as with pure samples. In all cases the maximum error due to analysis was less than 5%.

Preliminary runs, by means of imperfected operational procedures, indicated that about 2 hr. was required for attainment of steady state conditions. This period was progressively shortened, but usually several samples were taken (at half-hour intervals) to ensure the absence of any deviations from steady state conditions when data were being collected. These data indicated a mean reproducibility of all results, when analytical errors were included, of about ± 10%.

RESULTS

Conditions Studied

Table 1 compares the ranges of variables covered in this work with those used previously. In general, conditions which were studied extensively previously were not covered in detail in this work, and vice versa. Both resins used in this work were of the strong acid (polystyrene sulfonic) type, as the weaker IRC-50 carboxylic acid was shown previously to have little catalytic activity. In the production of Duolite resins additional steps are taken to provide a high degree of porosity (*1*), so that the final product may more nearly represent a usual catalyst rather than one having the continuous gel structure of other ion exchange resins.

Experimental Observations and Their Interpretation

The first series of runs was to determine whether the Reynolds numbers in the present work were sufficiently high to get entirely out of the region in which external, or gas-phase, mass transfer rates influence the results. At the same time it was desired to check the peculiar temperature effects observed earlier (*9*),

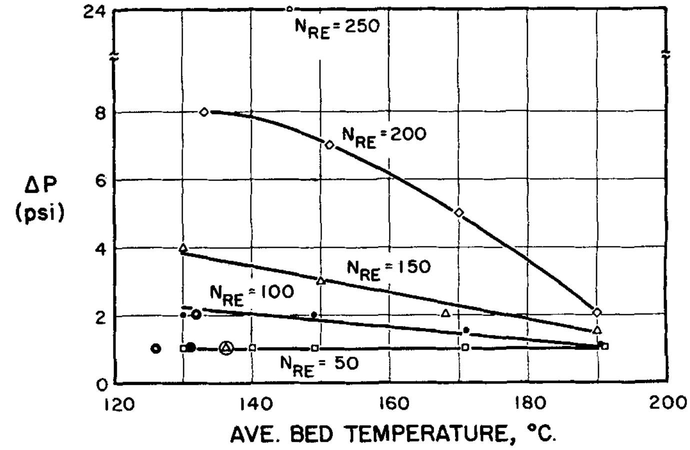

Fig. 2. Pressure drop across catalyst bed (symbols as in Figure 1).

where the rates were found to decrease with increasing temperature in the range up to about 150°C. As Figure 1 shows, the rates in the present study confirm the earlier effects of temperature observed in this region. More important there is clearly no consistent effect of Reynolds number, showing that complications due to external mass transfer effects are clearly absent. In the region above 150°C., temperature is seen to have little effect on the reaction rates. Clarification of this point will be possible in the light of other data later in the paper.

Figure 2 defines the peculiar pressure-drop effects observed in this system. At the higher flow rates the pressure drop through the bed becomes strongly dependent on temperature as well as on the Reynolds number. Normally only the small variations due to gas-density changes with temperature are expected (*10*, *13*), and these are in the opposite direction from the trends shown in Figure 2. Furthermore the pressure losses shown in Figure 2 become increasingly sensitive to flow rate as the flow rate increases. During the start-up, when superheated steam alone was passed through the catalyst bed, the pressure drops were always much less than those obtained when both steam and ethylene oxide were added to the catalyst bed. Further the pressure drops were extremely high; the bed depth corresponding to the data of Figure 2 was only about 2 in.*

To define clearly the reasons for the peculiar pressure-drop effects and thereby to develop a lucid picture of the catalyst structure under reaction conditions, several runs were made in a glass-walled reactor. These runs also served to obtain an estimate of the catalyst particle size during a run. The glass-walled reactor used to carry out the runs in which the particle size and structure under operating conditions were to be observed was a Jerguson gauge with a sight glass calibrated to determine the resin volume. The same start-up procedure was used as during the runs in the stainless steel reactor. After 25 ml. of wet resin was added to the Jerguson gauge, superheated steam was passed through the reactor. At an average bed pressure of 19 lb./sq. in. gauge and 141 °C. the resin volume shrank from 25 to 13.5 ml. (as compared to a volume of 17.2 ml. for air-dried resin and 13.0 ml. for oven-dried particles). When ethylene oxide (water/ethylene oxide mole ratio of 10) was added with the steam to the reactor at an average bed pressure of 13 lb./sq. in. gauge and 144°C., the resin volume increased to 14.8 ml. Not only did the volume of the resin change, but the appearance changed from a dry brown color when the superheated steam was passed through the bed to a moist (brown-sugary) appearance after the addition of ethylene oxide. Therefore the visual observations clearly indicated that the resin was sorbing large quantities of the components of the gas stream and as a result undoubtedly softening. As the temperature increases at constant total pressure, the quantities sorbed would decrease, hardening the resin and thereby decreasing the pressure drop. As a result of the softening at the lower temperatures, the pressure drop would serve to compact the bed and have a cumulative effect; the pressure drop, while low during start-up, compacts the bed slightly. This in turn further increases the pressure drop, resulting in further compaction, and so on, until finally at steady state the very high-pressure losses and great effect of flow rate shown in Figure 2 were obtained.

The most interesting series of runs were those that showed the effect of total pressure on reaction rates. An enormous dependence of the rates on total pressure was always observed, those of Figure 3 being typical. This dependence ranged from one of the second power of total pressure at the lower pressures to a fourth-power dependence as saturation pressures were approached at the other extreme. To determine whether these extraordinary pressure effects were due to changes in the partial pressure of ethylene oxide or that of the water, complete data were obtained at one temperature. Summarized by the solid lines of Figure 4, these data show approximately a first-power dependence of reaction rates on the ethylene oxide partial pressure. Therefore the enormously greater effects of total pressure must be due to changes in the partial pressure of water and therefore to its sorption by the resin. As conditions close to saturation are approached, the quantities of water sorbed should increase rapidly, thereby leading to the great effect of pressure shown in Figures 3 and 4. An alternate method of approaching saturation is that of decreasing the temperature at constant total pressure; if water sorption were the primary variable affecting reaction rates, then the lower the temperature the higher the reaction rate would become. This importance of water sorption is clearly confirmed by the data at 130° to 150°C. in Figure 1.

All rate data have been expressed in terms of the equivalents of acid catalyst. These rates may be converted to rates per mass or volume of catalyst by means of the following conversions: there are 4.14 equivalents per 1,000 g. (air dried) resin and 1.87 equivalents per 1,000 ml. of wet resin.

Development of a Quantitative Correlation

Correlation of the reaction-rate data must consider quantitatively the effects of water sorption described above. Quantitative water-adsorption data on ion exchange resins, at least at lower temperatures, have been reported by Sundheim, Waxman, and Gregor (*16*), and more completely by Glueckauf and Kitt (*8*). On the basis of these results the

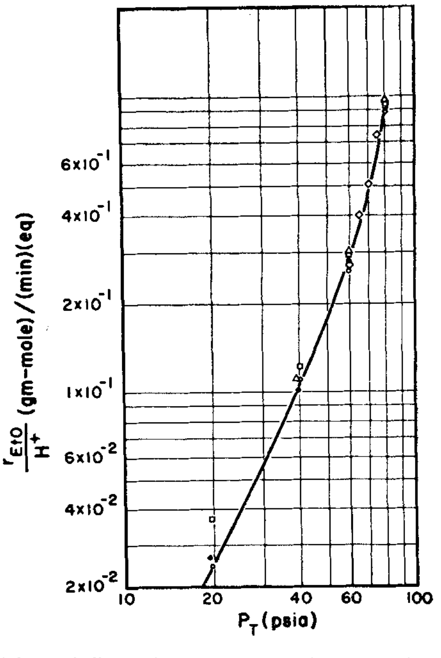

Fig. 3. Effect of pressure on ethylene oxide reaction rate: temperature, 160°C.; resin diameter, 0.78 mm.; water: EtO ratio, 15:1. Typical run conditions:

Symbol	N_{Re}	Selectivity
□	100	77.5–81.4
◇	200	78.8–84.2
▽	100	75.0–85.5
○	101	79.8–81.9
●	202	77.0–82.2

Selectivity expressed as the molal percentage of ethylene glycol in the product mixture of glycols.

TABLE 1. LEVELS OF EXPERIMENTAL VARIABLES

	This work	Hamilton and Metzner (*9*)
Modified Reynolds numbers	50 to 250	10 to 60
Total pressure	15 to 80 lb./sq. in. abs.	18 lb./sq. in. abs.
Catalyst types	Amberlite IR-120 and Duolite C-25	IR-120 and IRC-50
Catalyst particle diameters	0.088, 0.46 and 0.78 mm.	0.35 and 0.71 mm.
Temperature	130° to 190°C.	110° to 200°C.
Molar ratio of steam to ethylene oxide	5.08 to 20	7.5 to 32

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*The very high values of the pressure drop and the comparatively low values of the Reynolds numbers used are perhaps not quite so surprising when one considers the gas velocities used. In the present study gas velocities of up to 200 ft/sec. were employed. The Reynolds numbers are low in spite of these high velocities, since the diameter term is very small.

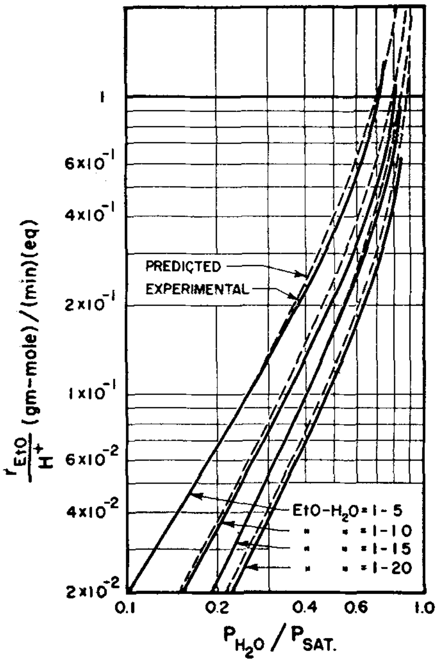

Fig. 4. Effect of pressure on reaction rates (summary).

B.E.T. (*3*) equation was chosen to represent the water-sorption isotherm:

$$v_{BET} = \frac{b(p_{H_2O}/p_{sat})}{[1 + a(p_{H_2O}/p_{sat})][1 - p_{H_2O}/p_{sat}]} \qquad (1)$$

The over-all rates must also be proportional to the total amount of catalyst used, or more specifically, to the equivalents of acidity which serve to catalyze the reaction. The final equation for reaction rates derived from these considerations may be written (at constant temperature) as

$$r_{EtO} = k'''(p_{EtO})(v_{BET})(H^+) \qquad (2)$$

Experimentally the variation of the rate constant with temperature could be described by an activation energy of 9.0 kcal./g. mole. Since this is identical to the latent heat of vaporization of water, an alternate statement of the same fact is that k''' varies with temperature in the same way as does the vapor pressure of water. Therefore

$$k''' = k''(p_{sat}) \qquad (3)$$

A combination of Equations (1) to (3) gives

$$r_{EtO} = \frac{k(p_{H_2O})(p_{EtO})(H^+)}{[1 + a(p_{H_2O}/p_{sat})][1 - p_{H_2O}/p_{sat}]} \qquad (4)$$

Figure 4 compares the rates predicted by means of Equation (4) with experimental results obtained at 160°C. The data cover a fourfold range of pressures and over a sixtyfold range of reaction rates. In view of the wide range of rates and the simple development of Equation (4), the fact that the results and predictions always agreed within about 20% (and usually better) is truly remarkable.

All the experimental data obtained, at all temperatures (130 to 190°C.), with the larger size particles are compared with Equation (4) on Figure 5 with coordinates suggested by the form of the B.E.T. equation used. The reciprocal of the rate constant is given by the intercept at a reduced pressure of zero; the slope of the line is equal to (a/k). Even from visual inspection alone it is evident that the only points which deviate by 15 to 20% or more are those runs for which the experimental scatter is greatest. The accuracy of the correlation is therefore more strongly limited by random errors in the data than by the form of the correlating equation. The mean deviation of points from the equation is 15%.

It is particularly noteworthy to consider that this correlation which uses a single set of values for a and k correlated the data over the entire 60°C. temperature range. This is equivalent to stating that not only is the rate constant correctly portrayed by Equation (3) but the sorption constants of Equation (1) are independent of temperature. A direct and independent check of this conclusion is available in the adsorption data of Glueckauf and Kitt (*8*) at somewhat lower temperatures; over a 25°C. range of temperatures the volumes of water adsorbed on a similar ion exchange resin changed only by between 6.5 and 0.7%, depending on the pressure used.

THEORETICAL INTERPRETATIONS

Of the usual steps which may influence the over-all reaction rates (chemical kinetics, sorption rates, internal and external mass transfer), only external mass transfer has been conclusively eliminated thus far. The correlating equations further show the extreme importance of water-sorptional effects, but exactly how these effects determine the over-all rates has not yet been established. For example, the sorption of water could possibly determine the rate of internal diffusion through the particle through its effect on particle size. Alternately, chemical kinetics could be rate controlling with the water sorption determining the activity of the protons which are responsible for catalysis of the reactions. The purpose of this section is to examine these questions and to consider the structure of the catalyst particle under reaction conditions in further detail.

Internal Diffusion and Conditions Within the Particle

To determine the importance, if any, of internal mass transfer rates (that is, diffusion within the particle) two additional types of experiments were carried out. In the first place runs with Duloite and Amberlite catalyst were made under identical conditions. The ethylene oxide reaction rates found were identical. Therefore one can conclude that either the Duolite was not porous under reaction conditions or that the porosity was not useful; that is the diffusion rates through the resin were as high as in the pores, or possibly diffusion rates were not limiting in any case. To check these findings the particle size of the Amberlite resin was changed from 0.78 to 0.46 and to 0.088 mm. The results given in Table 2 show that decreases in diameter indeed increased the rates, very nearly in direct proportion to the changes in surface area. The fact that the ratios of reaction rates are consistently slightly smaller than the measured ratios of diameters is felt to be due to the fact that the diameter ratios were measured prior to reaction; during startup a slight attrition always took place. This was more serious for the larger particles; hence the true diameter ratios under reaction conditions are somewhat smaller than the values of 1.68 and 8.8 reported. It is therefore concluded that the reaction zone was undoubtedly confined to a very thin region near the surface of the catalyst particles.

These conditions of surface reaction could have been caused by a low rate of diffusion of any one or more of the reactants or products through the catalyst particles. However the correlating equations clearly show no dependence of rate upon the partial pressure of ethylene glycol and of higher glycols in the gas phase around the particle. The rates of formation of the higher glycols were usually not great, but as the temperature, pressure, and Reynolds number were varied, the concentration of ethylene glycol in the gases leaving the reactor was varied all the way from saturation down to only a few percent of its saturation value. The absence of any effect of this variation upon the conversion rates clearly eliminates the possibility that diffusion of glycol through the particle may have been rate controlling. The same conclusion may be reached by noting that the formation rates of higher glycols were always low, and catalytic activity remained high. If much glycol had remained within the particle for an appreciable length of time, it would have the opportunity to react further with ethylene oxide to produce pro-

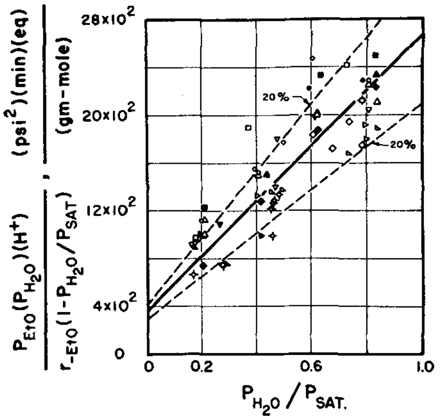

Fig. 5. Correlation of all data on 0.78 mm. catalyst particles.

Symbol	Reynolds number	Water: EtO molal ratio	Temperature °C.	Pressure lb./sq. in. abs.
-○-	210	10.4:1	150	35
-□-	190 220	10.3:1	130-190	35
◺	193-224	10.3:1	133-190	35
◣	89-103	15 4:1	130-191	35
▽	143-167	10.3:1	130-190	35
▼	48-56	10.3:1	130-191	35
▷	100	10.0:1	135	20-40
▶	200	10.0:1	135	21-40
●	100	10.0:1	160	19.7-80
○	203	10 0:1	160	19.7-80
△	100	15 0:1	160	19.5-80
▲	200	15.0:1	160	19.7-80
□	101	5.08:1	160	19.7-80
■	199	20.0:1	160	19.7-80
◇	101	15.2:1	160	59.8-74.8
◆	202	15.2:1	160	19.6-80

gressively higher glycols, eventually producing polyethylene oxide polymers which would completely plug or inactivate the catalyst. The fact that this did not occur is a further clear indication that both ethylene glycol and the higher glycols could diffuse from the scene of reaction rapidly in comparison to their rates of formation. Finally the rates should not have depended strongly on the ethylene oxide partial pressure if the diffusion of products was the rate-controlling step.* Further since water is probably the major adsorbed component in the gel (*9*) and its sorptional variations have been expressed through an equilibrium relationship, its diffusion rate may also be ruled out.

These arguments lead to the following conclusions:

1. The concentrations of water, glycol, and the higher glycols throughout the catalyst particle are essentially in equilibrium with the gas phase.
2. Internal diffusion of ethylene oxide may be at least partially rate controlling.

TABLE 2. EFFECT OF PARTICLE SIZE ON REACTION RATES

Runs	Temperature, °C.	Pressure, lb./sq. in. abs.	Ratio of diameters	Ratio of rates
47a and 68a	160	19.5	D_{47}/D_{68} = 1.68	$r_{68/47}$ = 1.16
47b and 67b	160	39.8	1.68	1.40
47a and 71a	160	19.5	D_{47}/D_{71} = 8.8	r_{71}/r_{47} = 7.9
47b and 71b	160	39.8	8.8	6.6

In the limiting case in which internal-diffusional resistances are very high, permitting only a very limited penetration of reactants into the resin, the rate expression is given by equations of the form (*7, 17*):

$$\text{rate per catalyst particle} = A(p_{EtO})\sqrt{kD_v} \qquad (5)$$

Therefore if ethylene oxide diffusion were entirely rate controlling, the large effect of partial pressure of water given by Equation (4) would be due to its influence on the square root term in Equation (5). It should be noted that Equation (5) predicts that the observed activation energy would be about half as great under diffusion-controlled conditions as that of the kinetically controlled reaction itself. The value found in the present work (the latent heat of vaporization of water or approximately 9 kcal./g.-mole) is exactly half the value reported for the liquid-phase acid-catalysed reaction (*12*).

Sorption Rates

Detailed arguments similar to those in the above section show (*6*) that if sorption rates were controlling, they could have been only the rates of ethylene oxide sorption. In this case the large effect of partial pressure of water could be explained by the assumption that ethylene oxide adsorption occurs primarily on wetted sites and therefore is a strong function of the number of such sites. Insufficient general information on the factors controlling these rates in systems of catalytic gels is available to confirm or to rule out such a rate-controlling mechanism.

Chemical Kinetics

In situations in which the chemical kinetics are slower than the other rate steps the reaction usually takes place rather uniformly throughout the entire particle. Since this is obviously not the case here, it is probable that this step was not rate controlling.

The single exception to complete particle utilization under kinetically controlled situations occurs when the reaction is confined entirely to the external surface of the particle, as in the case of a solid in which all diffusivities are essentially zero. If this were the case here, the rates should follow conventional kinetic relationships, including the usual large effects of temperature. Since the activation energies found in this work were only half as great as those of the liquid phase, acid-catalyzed reaction may quite probably be ruled out.

In summary all possible rate-controlling steps except ethylene oxide sorption and internal-diffusion rates have been ruled out with a considerable degree of certainty. As both of these mechanisms will fit the observed experimental data, no distinction between them is possible.

COMPARISON WITH PRIOR STUDIES

Choice of the B.E.T. equation to describe water adsorption in the present work has one unfortunate aspect due to the inherent limitations of the B.E.T. equation. As saturation conditions are approached, the equation breaks down, predicting infinite rates of reaction. As a result no extrapolation of the present data to liquid-phase conditions is possible, and the present data cannot be compared with those of Othmer and Thaker (*12*).

The differential rates obtained in the present study were several times as high as those obtained on Reed's (*15*) integral reactor, while the product-distribution range was approximately the same. The large effect of the amount of water in the resin on the reaction rates was observed but not fully recognized by Reed. The temperature variation throughout their integral reactor, as well as the absence of knowledge of their average particle sizes, prevents any more detailed comparison.

Duplication of several of the runs reported by Hamilton and Metzner (*9*) gave ethylene glycol rates that agreed within the small analytical error, while the diethylene glycol rates were very much lower in this work than in Hamilton's. The analytical procedure which was used previously for measuring the total glycol rates (dichromate-acid oxidation) was susceptible to errors due to polymer impurities in the feed, and since low conversions were obtained, these errors magnified the rates for the higher glycols. There appeared in Hamilton's studies to have been no appreciable effect of the partial pressure of ethylene oxide and temperatures above 150°C. on reaction rates. The small temperature effect on reaction rates for catalyst conditions far from saturation was confirmed by the present data, but the small effect of the partial pressure of ethylene oxide was not. A possible reason for the Reynolds number effect on the reaction rates found by Hamilton (and the small effect of the ethylene oxide) was that polymer in the feed was

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*This statement rests on the fact that ethylene oxide is the component adsorbed in the smallest quantities (*9*). If it were adsorbed in as large quantities as water, it could possibly influence product diffusion rates through its effect on particle swelling, hence the diffusivity of all components.

carried over and coated the resin, with the result that the rate-determining step became diffusion of ethylene glycol through the coated film. Further and conclusive evidence of resin coating in the previous study lies in the weight gain of Hamilton's catalyst particles during reaction and in the low activity of the used catalyst. In the present work, in which polymer entrainment into the reactor was eliminated, both the activity and appearance of the used and fresh particles were nearly the same, except for the highest temperature runs, in which some thermal degradation started to take place. Thus the earlier data (*9*) on ethylene glycol formation rates are confirmed herein, but resin activity (life) and the selectivity of glycol formation are both much higher than reported earlier.

PRACTICAL ASPECTS

This section presents preliminary information on factors of primary importance insofar as the commercial aspects of the reaction are concerned, as well as further scientific data.

Catalyst Life and Activity

The production of glycols was varied from 0.5 to 50 lb. of glycol produced/lb. of catalyst. The data (*6*) showed no trend in catalyst activity with time after the initial start-up. The resin activity rapidly decreased to about 85 to 90% of its initial activity and then remained at this level indefinitely.

Product Distribution

Detailed data (*6*) on selectivity of the catalyst toward formation of ethylene glycol (that is minimization of the formation of higher glycols) show that there is no trend with temperature, pressure, or Reynolds number. The variation with molal ratio of water to ethylene oxide is unusually slight, particularly when compared with the results reported by the prior art on sulfuric acid catalysts.

Effect of Conversion Level

The highest ethylene-oxide conversion studied was 54%, due to limitations of the equipment. (At higher conversion levels the temperature control was inadequate to cope with the high rates of heat release as the 54% conversion took place in a contact time of only 0.02 sec.) The products obtained under conditions of high conversion depend on the pressure and molal ratio of ethylene oxide to water in the feed stream. When both are low, conversion level does not appear to influence the product composition; that is 75 to 90% of the glycol mixture consists of ethylene glycol, just as at lower conversion levels. However the production of ethylene glycol may be nearly completely suppressed by running at pressures and molal ratios such that the reaction gases become supersaturated with respect to ethylene glycol. This suppression of ethylene glycol formation is not due to a loss of catalytic selectivity under such conditions but rather depends on the fact that the ethylene glycol formed has no place to go. Since it cannot leave the reactor so rapidly as it is being formed, it is converted into a mixture of higher molecular-weight glycols. Thus it is seen that the excellent selectivity of the present catalyst may either be exploited or masked completely by proper choice of the reaction conditions.

CONCLUSIONS

A mechanistic study of ethylene oxide hydration in the vapor phase over acidic cation exchange resins in a differential reactor showed that the rate-controlling step was either the diffusion rate of ethylene oxide into the catalyst particle or its rate of sorption onto the surface of the particle. The rate-controlling step is strongly influenced by the amounts of water sorbed by the catalyst. As a result the usual B.E.T. adsorption equation was used as a basis for quantitative correlation of the rate data.

No particular attempt was made to define all the factors which might conceivably affect the commercial aspects of this catalyst. However data obtained incidental to the above study showed excellent catalyst life and unusual selectivity over the entire range of variables studied.

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NOTATION

a = constant in B.E.T. adsorption equation
A = surface area
b = constant in B.E.T. equation
B.E.T. = Brunauer, Emmett, and Teller
D or D_p = particle diameter; numerical subscripts refer to run numbers
$Et(OH)_2$ = ethylene glycol
G = mass velocity based on empty cross-sectional area of reactor
$Hi(OH)_2$ = higher molecular-weight glycols (diglycol and up)
H^+ = equivalents of hydrogen ion (proportional to mass of catalyst used)
k''' = reaction-rate constant
k, k'' = proportionality constants in Equations (4) and (3) respectively (temperature-independent reaction-rate constants)
N_{Re} = modified Reynolds number for use in packed-bed calculations (*10, 13*), $N_{Re} = (D_pG/\mu)$
P, p = pressure, p_{EtO}, p_{H_2O}, p_{sat}, p_T refer to the partial pressures of ethylene oxide, water, the saturation (vapor) pressure of water, and the total pressure, respectively
r = reaction rate, r_{EtO}, reaction rate of ethylene oxide, moles per unit time; numerical subscripts refer to run numbers
v_{BET} = specific quantity of adsorbed water, as given by the B.E.T. equation
μ = viscosity of gas mixture passing through bed.

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