function of concentration and temperature (pressure) only. Even though these data include a threefold change in steaming rate, there is no steaming rate parameter. This is a condition of equilibrium.

Since carbon dioxide is formed in the hydrolysis of Na_2CO_3, equilibrium considerations indicate that increasing the pressure on the system would hinder the formation of NaOH. However, studies have shown that increasing the temperature increases the conversion. Since the system must be maintained in the liquid phase, high pressure is a necessary condition. Presumably, there may exist a temperature and pressure condition beyond which there can be no improvement in conversion. Such conditions actually do exist as is shown by the data in Figure 5. These data are for initially 1.0 and 2.5% Na_2CO_3 solutions and a steaming rate of 1000 ml./hr. and show that in most cases increases in temperature with the associated increases in pressure result in higher total conversion. However, for the 1% Na_2CO_3 solutions, while an increase in temperature from 410° to 550° F. and the resulting higher pressure improves the conversion considerably, further increase to 594° F. and 1000 p.s.i.g. results in no further advantage for the 1% Na_2CO_3 solutions.

Figure 5 also shows the effect of the initial concentration of carbonate on conversion at 593° F. and 1400 p.s.i.g. This is simply another means of looking at the data in Figure 3. Increasing the concentration from 1% to 2.5% equivalent Na_2CO_3 results in less than a twofold decrease in conversion. Conversion is not proportional to initial carbonate concentration because the NaOH concentration is different at different initial concentrations. As equivalent Na_2CO_3 concentration increases, conversion decreases in an exponential manner.

CONCLUSION

Equilibrium data for the thermal decomposition of concentrated sodium carbonate solutions have been obtained. Conversion of carbonate to caustic is limited by reaction equilibrium and depends on the volume of stripping gas. Optimum conditions exist, above which the increase in pressure associated with an increase in temperature inhibits further conversion.

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Thermal Conductivity of Porous Catalyst Pellets

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The effectiveness for reaction of the internal surface of a catalyst pellet depends upon the temperature and concentration profiles within the pellet. To evaluate the temperatures within pellets thermal conductivities must be known. Such information was measured by a comparative method for silver catalyst made by pelleting microporous powder particles. Data were obtained as a function of pellet density. The results showed very low conductivities [0.1 to 0.4 B.t.u./(hr. ft. ° F.)] in comparison with k_s for solid silver. Both micro and macro (spaces between powder particles) pores are shown to contribute to the low conductivity. Measurements as a function of pressure (1×10^{-2} – 760 mm. Hg.) suggest that free-molecule conduction is the primary mechanism of heat transfer in the micropores at pressures up to 760 mm. Hg. From these results it was estimated that the mean micropore size varied from 1500 to 5000 A. depending upon catalyst density.

IN 1955 Wheeler (*11*) estimated a temperature difference of 100° C. across the radius of an alumina catalyst pellet in an olefin hydrogenation reaction. Earlier Damkohler (*3*) had derived equations for estimating such temperature differences. Since then there has been considerable interest in the effect of temperature variations within the catalyst on the average rate of reaction for the pellet (*1, 2, 7*). The evaluation of the temperature profile depends upon the thermal conductivity of the porous material. Wheeler used a value of 0.24 B.t.u./(hr. ft. ° F.) which meant that the catalyst pellet was an insulating material and explained the large temperature difference. The small amount of data that has become available confirms the insulating properties of porous catalysts. Hence, it is particularly important that accurate values of k_e be known to determine the potentially large temperature gradients and their corresponding effect on the average rate of reaction per pellet. The objective of this investigation was to measure thermal conductivities for silver (high conductivity solid phase) catalysts for comparison with data for other materials. Such published data appears to be limited to the investigations of Sehr (*10*) and Mischke (*8*) on pellets made from low-conductivity solids. The first study presented a comparison of methods of measurement and single values of k_e for five different catalysts. Mischke determined the effective thermal conductivity for several densities of alumina pellets under both vacuum and atmospheric pressure with helium and nitrogen.

Experimental measurements (*6*, *9*) show that the rate of transport of mass by diffusion within a pellet is strongly dependent on the macropore volume, the void space surrounding the microporous particles of which the pellets are composed. The thermal conductivity is also a sensitive function of macropore volume or pellet density (*8*). On the other hand, the predominant part of the surface available for catalytic reaction is in the micropores, so that the surface area per unit mass is insensitive to changes in pellet density. Hence, the effectiveness of the interior surface of a catalyst pellet for reaction may be strongly dependent upon the resistance to mass and energy transfer through the macro pores. It is conceivable that catalysts of the future will be prepared with an optimum density to allow for transport resistances in the pores. For these reasons one of the primary variables studied in this investigation was macropore void fraction; data were measured over the range $\epsilon = 0.14$ to 0.61. The pore sizes in catalysts are small enough that free molecule conduction can be important. To evaluate this effect measurements were made with helium, air, and carbon dioxide in the pores at pressures from 1×10^{-2} to 760 mm. Hg.

EXPERIMENTAL WORK

Preparation and Properties of Powder and Pellets. Powdered silver catalyst particles were prepared by decomposing silver phthalate as described in diffusion studies on these materials (*6*). The method includes decomposition for 3 hours at 370° C. in a carefully dried stream of nitrogen, grinding the resulting material, and subsequent sieve analysis. The powder used was smaller than 200 and larger than 270 U. S. mesh size. X-ray diffraction analysis confirmed that the powder was crystalline silver in the face-centered-cubic form (observed reflection position: 38.2°, 44.4°, 64.7°, 81.6° and 98.1°). Within the sensitivity of the diffraction apparatus no silver oxide was detected. The properties of the powder are given in Table I.

Pellets of four different macropore void fractions were prepared by compressing the powder in a Carver Model B press. Different masses of powder were poured into a Lucite mould, 1.0 inch in I.D. In each case the powder was compressed to give a cylinrical pellet 0.50 inch in thickness, corresponding to a volume of 6.43 cc. From the known density of silver [10.5 gram/cc. (*4*)], and volume of the pellet, the volume fraction silver ϵ_s was computed. The micropore void fraction ϵ_m was established from the micropore volume (Table I). Then the macropore void fraction was obtained by difference:

$$\epsilon = 1 - \epsilon_s - \epsilon_m \tag{1}$$

These properties of the pellet are given in Table II. The macropore value, 0.144, for the most dense pellet is subject to some uncertainty by this method of calculation, but the results for the other pellets should be accurate. The low value for pellet No. 4 suggests that some deformation of the powder particles may have occurred at the high pressure required to form this particular pellet.

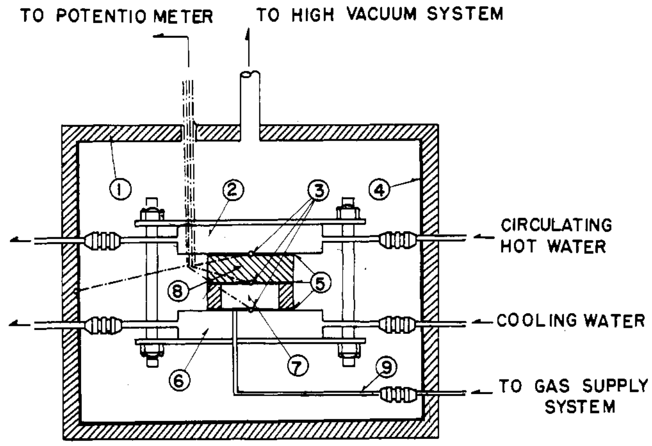

Figure 1. Diagram of equipment

Thermal Conductivity Apparatus. The thermal conductivity apparatus is shown in Figure 1. A comparative method is used, based upon using a reference material of known conductivity. As such, energy measurements were not required; however, the accuracy of comparative methods requires a reference material whose thermal conductivity is of the same general magnitude as that of the sample. For this work lucite [$k_L = 0.118$ B.t.u./(hr. ft. ° F.) at 25° C.] was employed.

The apparatus was similar to that used by Harper (*5*) except the surroundings of the cell were maintained in an outer vessel at a pressure of approximately 10^{-4} mm. Hg. The cell itself contained a heat source (*2*) and heat sink (*6*), the lucite reference block (*8*), 1.50 inches in diameter and 0.50 inch in thickness, and the lucite encased pellet (*7*), 1.00 inches in diameter and 0.50 inch in thickness. The energy was transferred to the lucite from the heat source through a sheet of silver (*5*), 0.5 mm. in thickness. Similar sheets were employed between reference lucite and pellet, and between pellet and heat sink. Their purpose was to give a relatively constant temperature in the radial direction at these three locations. The source consisted of a stainless steel cylinder through which hot water at a constant temperature (±0.01° C.) was circulated. The heat sink consisted of a similar hollow cylinder through which water at a temperature of 25° C. ±0.01° C. was circulated. The average temperature of the pellet was approximately 34° C. for all runs; the temperature difference across the

Table I. Properties of Microporous Silver Particles

Micropore volume, V_g	0.194	cc./gram
Surface area of micropore, S_g	25.8	sq. meters/gram
Mean micropore radius[a], $\bar{r}$	150 A.	
Approximate range of particle diameters	50-70μ	

[a] Determined from $\bar{r} = (2V_g/S_g)$.

Table II. Properties of Silver Pellets

Pellet No.	Pellet Weight, Grams	Bulk Density, Gram/Cc.	Volume Fraction[a] ϵ_s[b] silver	ϵ_m micropore	ϵ macropore	Total void $\epsilon_m + \epsilon$	Break-away Pressure (Air), Mm. Hg	Effective Width of Pore, A.
1	8.68	1.35	0.129	0.261	0.610	0.871	145	4950
2	13.1	2.04	0.197	0.395	0.408	0.803	175	4090
3	15.8	2.46	0.235	0.476	0.289	0.765	233	3050
4	19.0	2.96	0.282	0.574	0.144	0.718	468	1530

[a] Volume of pellet; 6.43 cc. [b] Based upon density of silver = 10.5 grams/cc.

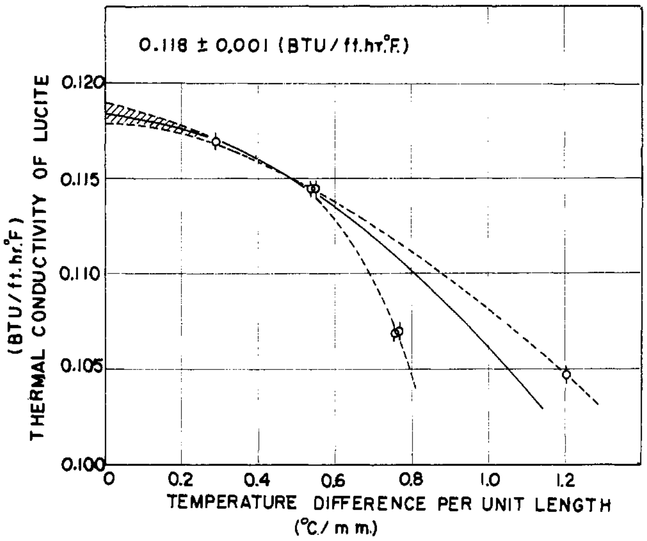

Figure 2. Thermal conductivity vs. water temperature difference

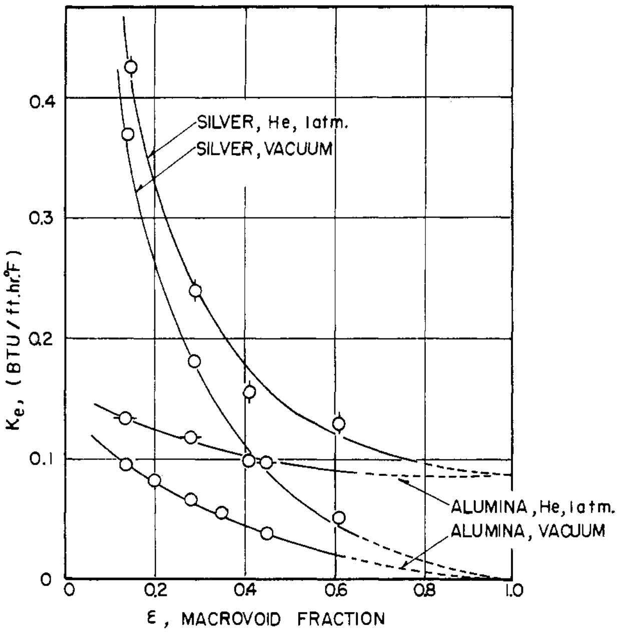

Figure 3. Effect of macrovoid fraction on thermal conductivity

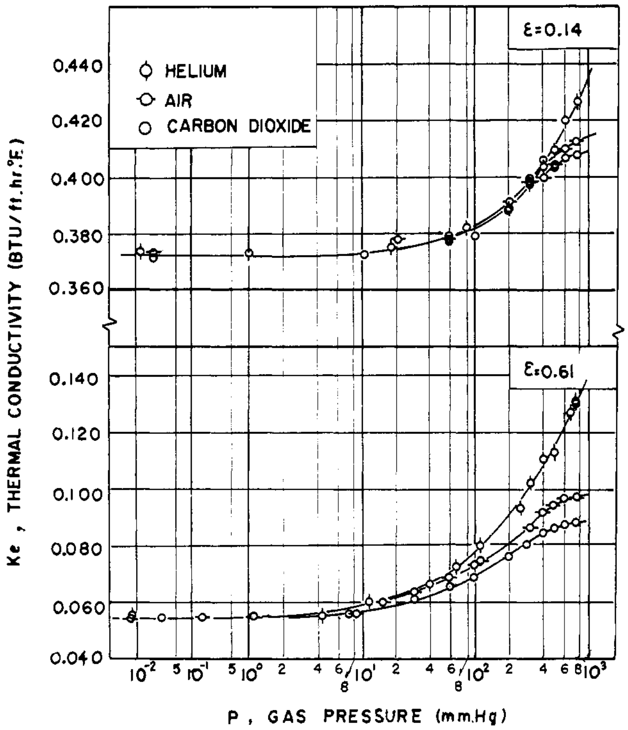

Figure 4. Effect of pressure

pellet varied from 15° to 20° C. A separate vacuum and gas supply system (*9*) was used to fill the pores of the pellet with helium, carbon dioxide, or air. The gas pressure was measured with a McLeod gage (from 8×10^{-3} to 25 mm. Hg) or with a mercury manometer (25 to 760 mm. Hg).

The outer shell (*1*) was a copper cylinder, 6 inches in diameter, whose inner wall was plated with aluminum. The high vacuum and aluminum were used to reduce radial heat loss from the lucite.

During a regular run, temperatures were measured at three points (*3*) at the center of the silver sheets dividing the heat source and lucite, lucite, and pellet, and pellet and heat sink. Copper constantan thermocouples (No. 30, U. S. gage wire) were welded to the silver sheets for these measurements.

Accuracy of Measurements. If there is no heat transfer from the cylindrical surfaces of the lucite, and if the temperature is uniform across the three silver sheets, the thermal conductivity k_e of the pellet is given by

$$k_e = k_L \left[1 + \frac{d_L^2}{d_c^2} \left(\frac{\frac{\Delta t_L}{\Delta L_L} - \frac{\Delta t_c}{\Delta L_c}}{\frac{\Delta t_c}{\Delta L_c}} \right) \right] \qquad (2)$$

where k_L is the conductivity of lucite, Δt and ΔL are temperature differences and distances in the direction of heat flow, and d refers to the diameter of the cylinders of lucite and catalyst (see nomenclature). This expression is the result of equating the heat transfer through the upper lucite cylinder to the energy transferred through the lower catalyst pellet and lucite ring.

To check the assumption of no heat loss from the cylindrical faces of lucite, preliminary measurements were made using a lucite cylinder to replace the pellet. Thermocouples were installed in the silver sheet, separating the two lucite pieces, at the center and at the radius. The maximum radial temperature difference observed was 0.27° C. By considering the effect of radial heat loss it is estimated that temperature differences of this magnitude could introduce a maximum error of 2% in k_e.

To evaluate k_L the same apparatus was used replacing the pellet with distilled water [k = 0.001429 cal./(sec. °C. cm.) at 20° C.; 0.001499 cal./sec. ° C. cm.) at 40° C. (*4*)]. With this arrangement the water was in the lower section of the apparatus, next to the cold sheet of silver (Figure 1). To minimize further natural convection in the water, measurements were carried out with successively lower temperature differences across the water. The results shown in Figure 2 plot the computed value of the conductivity of lucite *vs.* this water temperature difference. The value of k_L used for the subsequent work was obtained by extrapolating the data in Figure 2 to zero temperature difference. The result, 0.118 B.t.u./(hr. ft. ° F.) at 25° C., compares well with the value of 0.116 at 30° C. determined by Harper (*5*). The mean temperature of the lucite during the runs with catalyst pellets was about 40° C. Hence, some error is introduced in using 0.118 B.t.u./hr. ft. ° F. for k_L during

Table III. Experimental and Calculated Results

P = Mm. Hg
k_e = B.t.u./(Hr., Ft., ° F.)

Macropore void fraction, $\epsilon = 0.61$		$\epsilon = 0.41$		$\epsilon = 0.29$		$\epsilon = 0.14$	
P	k_e	P	k_e	P	k_e	P	k_e
Helium-Silver System							
760	0.130	760	0.154	760	0.241	763	0.426
760	0.130	700	0.154	600	0.237	600	0.420
700	0.126	615	0.141	400	0.221	500	0.408
500	0.112	400	0.136	300	0.215	400	0.403
400	0.111	300	0.131	200	0.203	300	0.396
320	0.101	200	0.125	85.5	0.190	200	0.388
250	0.092	60.0	0.113	60.0	0.186	82.0	0.380
120	0.078	30.0	0.107	11.2	0.182	60.0	0.377
70.0	0.071	8.5	0.101	1.20×10^{-2}	0.181	18.0	0.375
40.0	0.066	0.101	0.100			1.00	0.373
12.3	0.059					1.08×10^{-2}	0.373
4.21	0.054						
8.10×10^{-3}	0.054						
Air-Silver System							
760	0.097	760	0.141	760	0.224	760	0.412
600	0.094	600	0.140	500	0.220	590	0.409
500	0.094	500	0.139	300	0.214	500	0.404
400	0.091	400	0.137	200	0.207	400	0.399
300	0.085	300	0.133	100	0.197	300	0.398
120	0.074	200	0.128	60.5	0.190	200	0.390
100	0.072	105	0.118	50.0	0.188	60.0	0.378
60.0	0.068	60.0	0.110	1.60	0.178	20.0	0.378
30.0	0.063	20.0	0.106	8.0×10^{-3}	0.178	1.50×10^{-2}	0.373
15.6	0.059	10.0	0.104				
9.10	0.055	1.07×10^{-2}	0.100				
1.05	0.055						
0.150	0.054						
8.10×10^{-3}	0.054						
Carbon Dioxide-Silver System							
760	0.088	757	0.134	760	0.215	760	0.408
600	0.087	600	0.133	600	0.216	600	0.407
500	0.085	500	0.132	400	0.209	500	0.403
400	0.084	400	0.129	160	0.199	400	0.406
300	0.080	300	0.126	100	0.197	300	0.396
200	0.075	200	0.121	60.0	0.189	200	0.389
100	0.069	100	0.166	10.0	0.182	100	0.378
60.0	0.065	60.0	0.110	1.50×10^{-2}	0.183	60.0	0.377
30.0	0.061	30.0	0.107			9.80	0.372
8.30	0.055	7.01	0.102			1.05×10^{-2}	0.370
1.80×10^{-2}	0.054	0.310	0.102				
		1.06×10^{-2}	0.100				

the conditions of the runs. This error is expected to be low (less than 1%) due to the small effect of temperature on the thermal conductivities of solids.

RESULTS AND DISCUSSION

The experimental results are summarized in Table III for different pressures, gases, and pellet density (or macropore void fraction).

Solid Conductivity. The data at low pressures provide a measure of the conductivity of the solid phase in the pellet. These vacuum results are plotted *vs.* macro void fraction in Figure 3. For comparison the available information (*8*) on Boehmite ($Al_2O_3 \cdot H_2O$) is included. The surprising feature of the results are the low values of k_e for silver substances. Electron microscope photographs of the powder particles show that this material is an assembly of smaller particles. There will be high thermal resistances in the small areas of contact between these particles in the powder. This is apparent from the fact that the values of k_e extrapolated to zero macropore void fraction appear to be a small fraction of the conductivity of the solid phase itself. These extrapolated results should correspond to the conductivity of the powder particles.

The increase in k_e with decreasing macropore void fraction may be explained by the increase in contact area for heat transfer between powder particles. The larger and nonlinear increase for silver could result from the tendency of the softer silver particles to be bent and broken more easily, thus establishing a larger contact area. It is likely that the vacuum curves such as those shown in Figure 3 are dependent upon the size of the powder particles used to make the pellet; particularly, the intercept at $\epsilon = 0$ should be sensitive to this size.

Also included in Figure 3 are curves for pellets with the pores filled with helium at 1 atm. of pressure. These curves should extrapolate as $\epsilon \rightarrow 1.0$ to the thermal conductivity of helium gas. This is approximately 0.087 B.t.u./(hr. ft. ° F.). The effect of the gas, as measured by the difference between k_e under vacuum and atmospheric pressure, appears to be about the same for Al_2O_3 as for silver.

Sehr (*10*) measured values of k_e which ranged from 0.13 B.t.u./(hr. ft. ° F.) for platinum-on-alumina reforming catalyst pellets to 0.21 for silica-alumina cracking catalyst. The lack of void fraction data prevents comparing these values with the data given in Figure 3.

Effect of Pressure. Figure 4 illustrates the effect of pressure with data for the least and most dense pellets. The sharp rise in the curves with pressure is due to free-molecule conduction for which k_g is directly proportional to pressure. This occurs when the mean-free path is large with respect to the mean distance between macropore walls. In contrast, the conductivity of the gas becomes independent of p (for an ideal gas) when the pressure is large enough that the mean free path is small with respect to pore size. This is observed at about 400 mm. for the least dense pellet (ϵ = 0.61). Flattening of the curves occurs at a higher pressure for the most dense pellet (ϵ = 0.14) because the average pore size is smaller. The phenomenon is not noticed, even at pressures of 760 mm. for helium because the mean-free path for this gas is larger than that for air or carbon dioxide.

Data given in Figure 4 should permit the calculation of a mean distance $\bar{d}$ between pore walls in the macrovoid volume. One way of doing this is to evaluate the break-away pressure. First plots of the gas contribution to the conductivity $(k_e)_p - (k_e)_o$, *vs.* pressure were prepared. Then the break-away pressure is the intersection of the linear k_g *vs.* pressure line in the free molecule conduction region and the horizontal line in the normal conduction region. Figure 5 shows such curves for the most and least dense pellets using the air data. The value of $\bar{d}$ is obtained by calculating the mean-free path corresponding to the break-away pressure. The results tabulated in the last two columns of Table II indicate a decrease in mean macropore size from 4950 to 1530 A. as the macrovoid fraction of the pellet decreases. It is not possible to obtain pore-size distribution information for silver catalysts by the conventional mercury penetration method for comparison. However, such measurements for alumina pellets (*8*) over about the same void fraction range gave mean macropore diameters (assuming cylindrical pores) in the same range—i.e., from 9000 to 800 A. The pore-wall separation $\bar{d}$ is based upon a parallel plate concept and hence would be expected to be less than the pore diameter. Further, pore shape and structure may be different from solid to solid so that the diameter of equivalent circular pores would not be a function of void fraction alone.

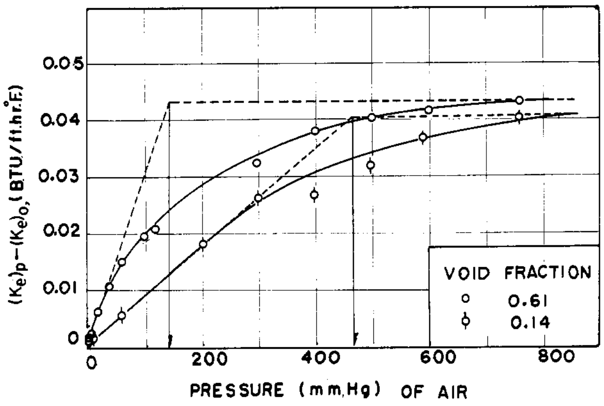

Figure 5. Break-away pressure lines

In summary, data have been determined showing the effect of gas pressure and kind of gas on the thermal conductivity of porous silver catalysts of different macropore void fraction. The large effect of macrovoid fraction on conductivity suggests that low-density pellets should be used if large temperature gradients are desired within the pellet. This might be desirable, for example, in the case of an exothermic reaction where higher internal temperatures would offset the decrease in rate of reaction due to pore diffusion resistances. Lowering the pellet density would also tend to reduce the diffusion resistance because of the accompanying increase in the pore size. In contrast, high-density pellets would be desirable for endothermic catalytic reactions, assuming again that the rate on the surfaces increases with temperature. High-density pellets would also be favored if undesirable side reactions occurred outside a narrow temperature range, or if catalyst activity was affected by large temperature changes.

The prediction of k_e for a pelleted catalyst will rest upon first being able to relate the thermal conductivity at zero macrovoid fraction to the conductivity of the solid phase. Additional information on the effect of the size of the microporous particles and their micropore size distribution is needed to hasten this development.

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NOMENCLATURE

d_L = diameter lucite reference sample, inches
d_c = diameter of catalyst pellet, inches
$\bar{d}$ = mean distance between pore walls, A.
k = thermal conductivity, B.t.u./(hr. ft. ° F.); k_L refers to lucite, k_e to effective conductivity of catalyst, k_g to gas, and k_s to solid
$(k_e)_p$ = effective thermal conductivity of catalyst with pores with gas at a pressure p; $(k_e)_o$ refers to gas pressure of about 1×10^{-2} mm. Hg; B.t.u./(hr. ft. ° F.)
ΔL_c = length of cylindrical catalyst pellet, 0.50 inch
ΔL_L = length of lucite reference samples, 0.50 inch
p = pressure, mm. Hg
$\bar{r}$ = mean radius of micropores, A.
S_g = surface area, sq. meters/gram
V_g = macropore volume, cc./gram
Δt = temperature difference; Δt_c = temperature difference across the catalyst pellet, Δt_L across lucite reference sample, ° F.
ϵ = volume fraction; ϵ_s refers to silver, ϵ_m to micropores, and ϵ to macropores

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