structural pattern of the film and the desired randomness.

2. A simple empirical procedure for finding such foreign atoms is to evaporate readily available commercial alloys of nickel and test their activity. The results of such a procedure are tabulated for batch hydrogenation of propylene in Table 1 as activities relative to nickel film at various conversion levels. The films prepared from nickel-chromium and nickel-chromium-iron alloys were the most active.

3. X-ray diffraction studies showed all films to be oriented in the $(1\bar{1}1)$ plane, but the nickel-chromium and nickel-chromium-iron films (the most active) showed some random orientation in agreement with the original hypothesis. Results were reproducible. Further studies could lead to even more randomly oriented and thus more active films.

4. The next step is the application of the findings of the film experiments to supported catalysts prepared by precipitation of mixtures of metal salts on kieselguhr followed by decomposition and subsequent reduction. It is postulated that nickel-chromium and nickel-chromium-iron supported catalysts will exhibit comparable superiority over nickel catalysts as that shown by the film studies. This work will be done, but these thoughts are presented here with the hope that other workers may be stimulated in employing orientation studies as a means of suggesting improved or new catalysts.

TABLE 1. ACTIVITIES OF VARIOUS NICKEL FILMS COMPARED WITH COMMERCIALLY PURE NICKEL FILMS

Conversion level	Film designation A	B	C	D	E	F
0.05	1.625	1.625	0.590	0.650	0.650	0.325
1.10	1.750	1.780	0.700	0.700	0.700	0.437
0.15	1.830	1.830	0.758	0.735	0.772	0.550
0.20	1.935	1.870	0.788	0.792	0.788	0.631
0.25	1.950	1.900	0.808	0.805	0.808	0.704

1. Activities expressed as ratio of reaction times at constant conversion for the pure nickel film to those of alloy film.
2. Designations indicate percentage of metal evaporated

A: 79.5 nickel, 13 chromium, 6.5 iron
B: 80 nickel, 20 chromium
C: 67 nickel, 30 copper, 1.4 iron, 1 manganese
D: 66 nickel, 29 copper, 2.75 aluminum, 0.9 iron
E: 95.5 nickel, 4.5 manganese

EXPERIMENTAL METHODS

Briefly, the films were evaporated from a tungsten filament to a 500-ml. flask with nickel and nickel-alloy wires wrapped around the helical filament. Other significant data include:

Vacuum:	0.1μ
Flask wall temperature:	103°F.
Current:	30 to 32 amp. at 10 v.

The reaction was carried out in the flask without prior contact with the atmosphere. Pretreatment for 6 hr. with hydrogen or propylene eliminated the induction period and permitted comparison of films on an equal basis.

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The Effect of Velocity Profile on Axial Dispersion in Packed Beds

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To my knowledge no treatment of axial dispersion in packed beds which accounts for the effect of the velocity profile has been published. Yet it seems possible that some of the axial dispersion observed in packed beds is caused by the combined influence of velocity profile and radial diffusion. Consider a pulse of dye flowing through a packed bed. The variation of axial velocity with radius causes the pulse to spread axially; however radial diffusion counteracts this by causing the dye that has been carried ahead in the faster flow to diffuse radially into slower flow, and likewise dye that has been held back in the very slow flow diffuses into faster flow. As the ratio of the bed diameter to the particle diameter is increased, these two counteracting effects vary as follows. The velocity profile becomes flatter and tends to cause less dispersion. The radial diffusion is also reduced because the particles are smaller in relation to the radius of the bed. This however tends to cause more dispersion. The following work is an attempt to evaluate these effects by calculating the N_{Pe} from a theoretical development similar to that used by Taylor (*1*) to evaluate these effects in pipe-line flow.

A material balance around a differential annular shell that moves with the mean superficial velocity of the stream yields

$$\frac{\partial}{\partial z}\left[zE\left(-\frac{\partial c}{\partial z}\right)\right]$$

$$+ zR^2(u-U)\frac{\partial c}{\partial x} + zR^2\frac{\partial c}{\partial t} = 0 \qquad (1)$$

Although the consideration of axial convection and radial diffusion is a two-dimensional problem, the resulting axial dispersion is only one-dimensional. The transition is obtained mathematically through using an effective axial diffusivity and writing material balances [Equations (2) and (5)] where axial convection and radial diffusion are replaced by an imagined axial diffusion. The next equation is obtained from a material balance around a cylindrical element which moves with the mean superficial velocity of the stream and is of differential length dx and finite radius R:

$$\frac{\partial}{\partial x}\left[\epsilon\left(-\frac{\partial \bar{c}}{\partial x}\right)\right] + \frac{\partial \bar{c}}{\partial t} = 0 \qquad (2)$$

When one assumes $\partial\bar{c}/\partial x$ to be constant, Equation (2) shows that $\partial\bar{c}/\partial t = 0$; when one assumes $\partial\bar{c}/\partial t = \partial c/\partial t$, Equation (1) becomes

$$\frac{\partial}{\partial z}\left[zE\left(\frac{\partial c}{\partial z}\right)\right] = zR^2(u-U)\frac{\partial c}{\partial x} \qquad (3)$$

When one assumes that $\partial c/\partial x$ is constant, the integration of Equation (3) gives

$$c - c_o = (\partial c/\partial x)\int_0^z \frac{1}{Ez'}\int_0^{z'} R^2(u-U)\,z''\,dz''\,dz' \qquad (4)$$

These assumptions apply rigorously only when radial diffusion is so fast compared with axial convection that there is no axial dispersion. When there is no dispersion, $\partial c/\partial t = 0$, $\partial c/\partial x$ = constant (where x is a coordinate that moves with the mean superficial velocity of the stream), and $c \neq c(z)$. In essence the above development relaxes the last restriction and yet holds the first two. Therefore the solution applies only when the time for flow is much greater than the time for decay of the radial concentration gradient due to diffusion. Taylor showed that this is equivalent to

$$\frac{L}{u} >> \frac{R^2}{\mathcal{D}(3.8)^2}$$

In McHenry's (2) equipment, which provides the only experimental data for the comparison with this work, L/u = 1 to 3 sec. when u = 1 ft./sec. and $R^2/\mathcal{D}(3.8)^2$ = 0.42 sec. Hence the validity of the above assumptions needs experimental verification but is not obviously false.

The net flow of tracer through a disk that forms a boundary of the tracer pulse at the inlet and which moves with the mean superficial velocity of the stream is given by the following two expressions.

$$2\pi R^2\int_0^1 (u-U)\,cz\,dz = -\epsilon\pi R^2\frac{\partial c}{\partial x} \qquad (5)$$

By substituting Equation (4) for c in Equation (5) one obtains the following equation, thus permitting the evaluation of the effective axial diffusion coefficient.

$$\epsilon = -2R^2U^2\int_0^1\left(\frac{u}{U}-1\right)z \int_0^z \frac{1}{Ez'}\int_0^{z'}\left(\frac{u}{U}-1\right)z''dz''dz'dz \qquad (6)$$

(Note: $\int_0^1 (u-U)c_o z dz = 0$)

ϵ was evaluated from Equation (6) by numerical integration, with the velocity profiles measured by Collins (3) used. The experimental velocity measurements were extended beyond z = 0.95 with the following correlation:

$$\left(\frac{u}{U}\right)_o - \frac{u}{U} = a + b\ln(1-z) \qquad (7)$$

The radial Peclet number was assumed to be 10, and the radial diffusivity was evaluated from

$$E = \mathcal{D} + \frac{\delta_p u}{10} \qquad (8)$$

The results of these calculations are summarized in Table 1.

TABLE 1

D/δ_p	Re	f†	N^*_{Pe}, calc.	N^*_{Pe}, exp.[2]
10.7	221	.37	3.2	
15.7	200			1.85
16.0	147	.36	1.7	
21.3	110	.35	10.4	

† Estimated from reference 4.

The resulting N^*_{Pe} do not vary monotonically with D/δ_p because of the offsetting effects of velocity profile and radial diffusion. D/δ_p was varied experimentally by Collins by using 3/8, 1/4, and 1/16-in.–diameter spheres in a 4-in.–diameter bed. The velocity profiles corresponding to the 3/8 and 1/4-in. spheres show little change; yet E [Equation (8)] is smaller for the 1/4-in. spheres, and hence the N^*_{Pe} is lower. The velocity profile for the 1/16-in. spheres is flatter, hence the higher N^*_{Pe}.

The agreement between the calculated value at D/δ_p = 16 and the experimental value is probably fortuitous because the theory is based on the assumption that axial dispersion is small, and the velocity near the wall, not well known in this case, has a strong influence on the result (5). Nevertheless this analysis does show that N_{Pe} is a function of D/δ_p in beds where the velocity profile is not flat. Although this analysis does not yield information about the dependence of N_{Pe} on the radial position, the action of the velocity profile might bring about such a dependence.

NOTATION

a, b = experimental constants
c = concentration
$\bar{c}$ = mean concentration = $2\int_0^1 cz\,dz$
D = bed diameter
E = radial diffusivity
f = void fraction
L = length of bed
N_{Pe} = Peclet number based on the mean superficial velocity
N^*_{Pe} = Peclet number based on the mean interstitial velocity
o = center line
R = bed radius
R_e = Reynolds number based on the particle diameter
t = time
u = point superficial velocity
U = mean superficial velocity
x = spatial coordinate along the axis of the bed
z = r/R where r varies between 0 and R
δ_p = diameter of the particles
$\mathcal{D}$ = molecular diffusivity between the tracer and the carrier gases
ϵ = effective axial diffusivity

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