subject felt calm. Within 2 minutes the hallucinations were gone, as was the nystagmus, and the pupils were normal in size. Eleven minutes later he said, "Even at the height of this, my mind felt better and more pleasant than usual." There was no significant change in blood pressure or pulse during the experiment.

The fifth observation was made on the second subject who had received 2 mg of bufotenine 90 minutes previously. On this occasion he received 16 mg of bufotenine I. V. Almost immediately he reported a burning sensation in the roof of his mouth. His face turned a livid purple, and he experienced generalized tingling of the body. During the second minute of injection his pupils were in wide dilation, and the ceiling of the room appeared "fuzzy" to him. During the third minute of injection he retched and vomited and stated, "My chest feels crushed." As the needle was withdrawn, marked mydriasis and nystagmus were noted. At that time, he saw red spots passing before his eyes and red-purple spots on the floor, and the floor seemed very close to his face. Within 2 minutes these visual phenomena were gone, but they were replaced by a yellow haze, as if he were looking through a yellow lens filter. Attempt to subtract serial 7's from 100 was abandoned because of many errors. His face remained deeply purple and sweating was profuse.

Nine minutes after the beginning of the experiment he stated, "Words can't come. I can't express the way I feel. My mind feels crowded." The pupils assumed normal size, but the nystagmus persisted for 30 minutes longer. At the 12th minute there was a fleeting return of the red spots before his eyes. At the 16th minute he said, "When I start on a thought, another one comes along and clashes with it, and I can't express myself clearly," and at the 25th minute, "I feel dopey but not sleepy. I feel physically tense and mentally clouded. I am here and not here." Time and space perception were grossly impaired, the yellow haze persisted, and his face remained purple. After 40 minutes he was able to report, "I feel better, but I still feel like I want to walk it off—like a hangover." His face assumed its normal color at the end of an hour. No significant change in pulse or blood pressure occurred throughout the experiment.

These observations indicate that slow (3-min) I. V. injection of bufotenine is feasible in healthy young males in quantities as high as 16 mg without jeopardizing life, that the drug is hallucinogenic, that there is a linear progression in symptoms as dose increases, and that its effects are reminiscent of LSD_{25} and mescaline but develop and disappear more quickly, indicating rapid central action and rapid degradation of the drug. The presence of nystagmus and mydriasis provokes the thought that at least a portion of its effect is localized in the brainstem tegmentum. There is surprisingly little cardiovascular effect; neither systolic nor diastolic blood-pressure changes exceeded 14 mm-Hg throughout these observations, and pulse rates never varied more than 12 beats per minute. If the color of an eggplant were diluted, it would approximate the unique purple hue of the faces of these subjects, which may be due to a serotoninlike bronchiolar constriction and consequent anoxemia. Serotonin does not produce transient model psychoses of this type, but the possible role of anoxemia in the production of the hallucinogenic effects of bufotenine requires clarification. These studies will be expanded.

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Stepwise Reaction via Intermediates on Separate Catalytic Centers

In heterogeneous catalysis an observed chemical reaction may take place via consecutive steps involving one or more real reaction intermediates. The term *real* shall distinguish them as existing as desorbed species in finite concentration; they may or may not be observable with given analytic methods. In porous, solid catalyst particles, the fate of such intermediates is determined by chemical kinetics as well as by the laws of diffusive transport (*1*). If individual reaction steps require different kinds of catalytic sites, the over-all reaction rate will be influenced by the diffusive transport velocity of the respective intermediates between such different sites. We will be interested in the ability of such a catalyst system to catalyze the over-all reaction, especially when the partial pressure of intermediates is very small.

It is possible to formulate quantitatively the requirements for geometric intimacy of the different catalyst materials to obtain an over-all reaction rate unimpeded by transport difficulties of the intermediates.

For an ordinary single step reaction, $A \rightarrow B$, following arbitrary reaction kinetics, a general condition can be derived for having the reaction rate uninhibited by diffusion effects. We shall consider a given catalyst particle (pellet, granule, or the like), with essentially all reaction sites located within the pore structure, and approximated by a sphere of radius R_o. The rate of reaction from the entire particle per (external geometric) particle surface, $\mathrm{d}N_s/\mathrm{d}t$, must equal the net diffusive flux across its boundary

$$\frac{\mathrm{d}N_s}{\mathrm{d}t} = D_{\mathrm{eff}} |\mathrm{grad}\ C|_{R=R_o} \qquad (1)$$

where C is the reactant concentration and D_{eff} is the effective internal diffusivity. For negligible inhibition of the reaction rate by diffusion, we require a negligible internal loss of reactant concentration; that is,

$$|\mathrm{grad}\ C|_{R=R_o} \ll \frac{C_o}{R_o} \qquad (2)$$

where C_o is the external reactant concentration. This condition, together with Eq. 1, results in the criterion

$$\frac{1}{3}\frac{\mathrm{d}N_v}{\mathrm{d}t}\frac{1}{C_o}\frac{R_o^2}{D_{\mathrm{eff}}} \ll 1 \qquad (3)$$

in which we have introduced the observed reaction rate per unit particle *volume*, $\mathrm{d}N_v/\mathrm{d}t = 3\ \mathrm{d}N_s/R\ \mathrm{d}t$.

For a reaction of *n*th order—that is, $\mathrm{d}N_v/\mathrm{d}t = aC^n$—a given internal concentration decrease will result in a smaller effect on the rate, the smaller n is, since

$$\mathrm{d}\left(\frac{\mathrm{d}N_v}{\mathrm{d}t}\right) \Big/ \frac{\mathrm{d}N_v}{\mathrm{d}t} = n\,\frac{\mathrm{d}C}{C}$$

However, Wheeler (*2*) has pointed out how even for the zero-order reaction inhibition by diffusion effects will result: The reaction rate must begin to vanish at some finite or, at least, at zero concentration; inhibition becomes noticeable when the reactant concentration at the particle center reaches such minimum or zero value. Following Wheeler's rigorous solution of the zero-order case, we can show that this condition obtains when

$$|\mathrm{grad}\ C|_{R=R_o} = 2\,\frac{C_o}{R_o}$$

Thus, even for the extreme case of zero-order kinetics, the condition 2 and, therefore, the theorem 3 are not altered by more than a factor of 2. We may accept this condition as sufficiently independent of detailed reaction kinetics.

A reaction $A \rightarrow C$ shall now proceed via intermediate products B and B',

$$A \xrightarrow{\text{O}} B \xrightarrow{\bullet} B' \xrightarrow{\text{O}} C$$

The reaction steps $A \rightarrow B$ and $B' \rightarrow C$ proceed on catalyst type O, and the reaction $B \rightarrow B'$, on catalyst type ●. The catalyst consists of a mixture of porous particles of each catalyst type, having a size approximated by a spherical radius R_o.

The reaction will now be uninhibited by diffusion transport if *each reaction step fulfills the condition 3.* For the steady state the reaction rate of each reaction step must equal the observed over-all reaction rate of the catalyst composite dN_v/dt. Therefore,

$$\frac{1}{3}\frac{dN_v}{dt}\,\frac{1}{C_i}\,\frac{R_o^2}{D_{\text{eff}}} \ll 1;\ i = A, B, B' \qquad (4)$$

It is obvious that it suffices to satisfy this condition for the intermediate existing at the lowest concentration. The criterion (*3*) demonstrates the increasing "intimacy" requirements, in terms of particle size of the catalytic components and their internal diffusivity, since intermediate species at decreasing partial pressure are relied upon for propagation of the reaction. The following will indicate some consequences of this finding.

In typical hydrocarbon reactions over oxide catalysts, the order of magnitude for the over-all reaction rate is about $dN_v/dt = 10^{-6}$ (moles per second per cubic centimeter of catalyst). (This corresponds to 50-percent conversion at a space velocity of about 1 weight of reactant per weight of catalyst per hour). The gas phase concentration C_i of any reacting species is about $10^{-5}\,P_{\text{atm}}$ (moles per cubic centimeter), when expressed in terms of its partial pressure P_{atm}. Condition 3 therefore becomes

$$\frac{R_o^2}{D_{\text{eff}}} \ll 30\,P_{\text{atm}}$$

The diffusivity of catalyst materials can be estimated from other physical constants (*2*) or can be measured directly (*3, 4*). On a typical gel-derived oxide catalyst of about 150 m^2/g surface area, we find the diffusivity at 450°C for hydrocarbon of 100 molecular weight to be about 2×10^{-3} cm^2/sec. For this type of catalytic material and the afore-mentioned reaction conditions, we obtain for the critical particle size

$$R_c \leqq 0.24\sqrt{P_{\text{atm}}} \qquad (5)$$

An upper limit to the partial pressure of a proposed true intermediate is set by thermodynamics. A test for the feasibility of the reaction system can therefore be made with P_{atm} calculated from thermodynamic constants alone.

For example, at a partial pressure of the intermediate specie of 10^{-3} atm—as might apply to the thermodynamics of olefin production accompanying a hydrocarbon reaction—a maximum particle size of about 50μ would be indicated.

It is interesting to note that an intermediate specie existing at a partial pressure as low as 10^{-10} atm could propagate a heterogeneous stepwise reaction if the adjoining regions of activity are of near 100-A dimensions.

In liquid media—for example, biological systems—the afore-mentioned criteria should be applicable to reaction systems where different catalyzed processes take place in distinct but adjoining regions of volume via diffusing intermediates. With typical magnitudes for diffusivity in liquids ($D_{\text{eff}} \approx 10^{-6}$ cm^2/sec), we have, for example, for 100-μ sized regions, an uninhibited reaction rate (in moles per second per cubic centimeter of space) of $10^{-2}\,C_i$, where C_i is the concentration of the intermediate in moles per cubic centimeter.

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Convenient Method for Recognizing Nonopaque Cerium Earth Minerals

The property of discontinuous absorption of visible light by neodymium and praseodymium in nonopaque cerium earth minerals has been used by Wherry (*1*), Mertie (*2*), Adams (*3*), and others as a means of identifying these minerals. The very sharp absorption of yellow light (570 to 590 mμ) by neodymium is especially useful and can be readily observed by illuminating the mineral with white light and looking at either the reflected or transmitted light through a visual spectroscope. Such spectroscopic observations, as well as the usual determinations of refractive indices under oils, become very tedious, however, when a large number of monazite concentrates have to be checked for contamination by similar appearing minerals, such as epidote or xenotime, or when concentrates of other minerals must be checked for freedom from monazite or other cerium earth minerals. Doubtful grains must then be carefully isolated and tested individually.

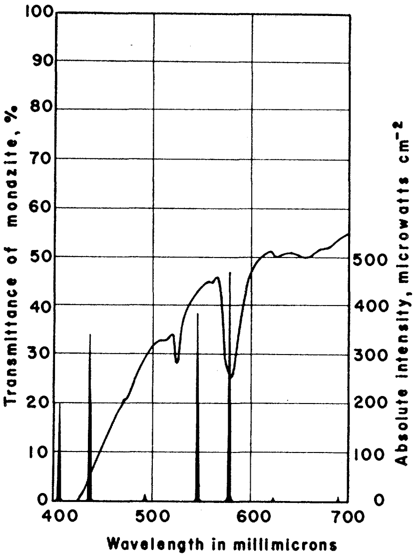

Fig. 1. The four vertical lines represent the main spectral-line emissions of a medium-pressure mercury-vapor arc in the visible region. The curve indicates the transmittance of a thin section of a monazite crystal.

The method developed (*4*) uses the same strong absorption of yellow light by neodymium as does the method of spectroscopic observation but in quite a different way. The sample is illuminated with the unfiltered light of a medium-pressure mercury-vapor lamp rather than with white light, and under this special light cerium earth minerals assume a characteristic emerald color, whereas other minerals undergo little change in color. A low-pressure quartz mercury-vapor lamp may also be used, provided that the purple filter, which is usually attached to such a lamp to eliminate visible radiation, is removed and a piece of ordinary glass is attached to eliminate the harmful 253 mμ ultraviolet radiation.

Figure 1 gives the optical data necessary to explain the principle of the method. The four main spectral-line radiations emitted by a medium-pressure mercury-vapor lamp (*5*) have been drawn at their respective wavelengths along the abscissa, and the height of the lines is proportional to their intensity of emission. The irregular curve shows the relationship between transmittance and wavelength for a thin section of a monazite crystal from Hittero, Norway, cut normal to the *c*-axis. This curve is typical of cerium earth minerals in general and shows a general absorption of all wavelengths shorter than about 440 mμ and the characteristic absorption of yellow light (570 to 590 mμ) ascribable primarily to neodymium.

The violet radiation (405 mμ) and the blue radiation (436 mμ) of the lamp lie in the region of general absorption and