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

$$A \overset{\mathrm{O}}{\rightarrow} B \overset{\bullet}{\rightarrow} B' \overset{\mathrm{O}}{\rightarrow} C$$

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,

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

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 $10^{-5}\,P_{\mathrm{atm}}$ (moles per cubic centimeter), when expressed in terms of its partial pressure P_{atm}. Condition 3 therefore becomes

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

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

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

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 ($D_{\mathrm{eff}} \approx 10^{-6}$ 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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3 November 1955

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.

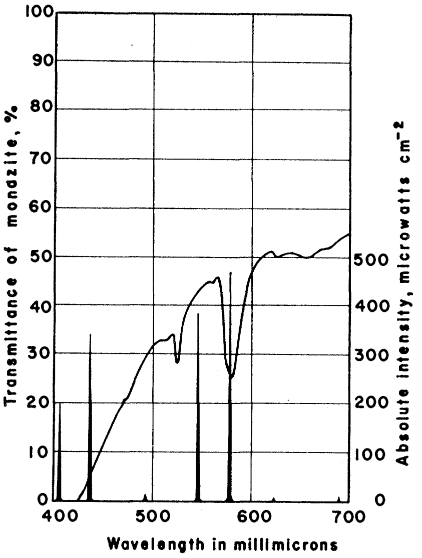

Fig. 1. The four vertical lines represent the main spectral-line emissions of a medium-pressure mercury-vapor arc in the visible region. The curve indicates the transmittance of a thin section of a monazite crystal.

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 are strongly absorbed. The removal of these two radiations in this manner is not unique to cerium earth minerals, for most yellow, orange, or red minerals would do likewise. The yellow radiation (578 mμ), however, lies well within the strong absorption band of neodymium. This radiation emerges greatly weakened from a thin section or a grain of a cerium earth mineral, whereas the green radiation (546 mμ) is relatively little affected, because it lies in an adjacent spectral region of relatively high transmittance. The net result is that cerium earth minerals assume the emerald color of the unabsorbed component, whereas other minerals, more or less, retain the color that they have under white light. Nonopaque, nonmetamict cerium earth minerals are the only ones known to us that have the requisite absorption properties to produce this effect, so the test appears to be highly specific. The samples are observed directly with the naked eye without recourse to a spectroscope, thereby greatly simplifying the task of recognizing cerium earth minerals in mineral concentrates.

The principle of the method should be applicable to the identification of any mineral that has a strong, narrow band in its absorption spectrum. A light source emitting only two wavelengths of visible radiation would be devised, one wavelength being selected to lie within the absorption band and the other to lie nearby on either side of the band in a region of low absorption. The mineral would assume the color of the unabsorbed radiation.

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Hemoglobin J

Previous reports have defined nine abnormal human hemoglobins that differ in their physicochemical properties, and several summaries of the literature to date are available (*1, 2*). Two of the abnormal hemoglobins described, H (*3*) and I (*4*) have been found to have a higher electrophoretic mobility at a *p*H of 8.6 than normal adult hemoglobin (*5*). The subject of this report is a third such hemoglobin that migrates more rapidly than normal adult hemoglobin at *p*H 8.6 but has electrophoretic properties differing from hemoglobins H and I. We propose that this hemoglobin be assigned the letter J for purposes of identification (*6*).

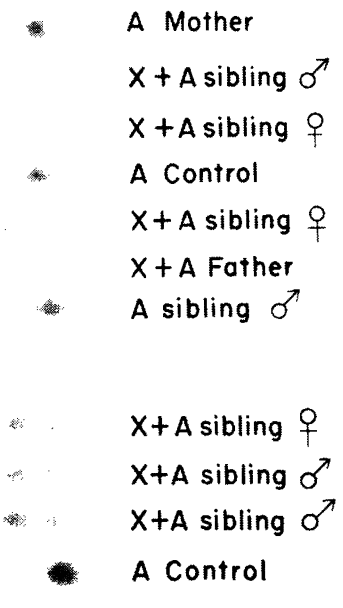

Fig. 1. Comparison by filter-paper electrophoresis of hemoglobin solutions from members of the family under study with normal control in Veronal buffer of *p*H 8.6 and approximate ionic strength of 0.025. Migration is to the left.

This hemoglobin was found in a young Negro female with bilateral cystosarcoma phyllodes. It was first identified by paper electrophoresis using the apparatus described by Smith and Conley (*7*) with Veronal buffer at *p*H 8.6 and approximate ionic strength of 0.025 (Fig. 1). Blood from 13 other members of the family has been examined, and the abnormality has been found in seven (Fig. 2). The father and six of nine siblings, including the propositus, had this component in addition to normal adult hemoglobin. The presence of previously described abnormal hemoglobins could not be detected. A search for the presence of the sickling phenomenon and fetal hemoglobin was unrewarding. The scatter of this family over the eastern seaboard curtailed the number of studies that could be made.

In four patients with the abnormal hemoglobin, dry smear morphology could be examined; in these instances it appeared normal. Hematocrits were obtained on all members of the family and were normal. Fragility studies were obtained in six instances of the abnormality and were normal in each case. Bilirubin was normal in the four instances in which it was obtained. None of the family had historical evidence of hematologic difficulties, and physical examination of those who were available to us failed to reveal abnormalities that were attributable to this abnormal component.

This hemoglobin component was further studied by moving-boundary electrophoresis, and its uniqueness was established by comparison with hemoglobins H (*3*) and I (*4*), the other hemoglobins that have higher mobilities than hemoglobin A at *p*H 8.6. Moving-boundary electrophoretic analyses were conducted with naturally occurring mixtures of hemoglobin A with H, I, and J (*8*). Differences were established by comparison of the migration of the abnormal hemoglobin boundaries with that of hemoglobin A. Univalent buffers of ionic strength 0.1 were used. The buffers were as follows: *p*H 6.5 cacodylate, *p*H 7.8 barbital, *p*H 8.6 barbital, and *p*H 9.8 glycine. Each buffer was $0.08M$ in sodium chloride and $0.02M$ in the sodium salt of the buffer. At *p*H 6.5 hemoglobins A, I, and J migrated as cations, and hemoglobin H as an anion; at *p*H 7.8 and higher, all four forms migrated as anions.

In each of the buffers, the mobility of hemoglobin J was between those of hemoglobins A and I, the mobility difference between A and I being 0.6 to 0.7×10^{-5} $\mathrm{cm^2\,sec^{-1}\,v^{-1}}$ and that between A and J 0.3 to 0.4×10^{-5} $\mathrm{cm^2\,sec^{-1}\,v^{-1}}$. The specimen containing hemoglobins A and H was also examined in cacodylate chloride buffer of *p*H 6.2. The mobility difference between A and H had a large *p*H dependence (*9*), increasing from 1.0 to 2.6×10^{-5} $\mathrm{cm^2\,sec^{-1}\,v^{-1}}$ between *p*H 9.8 and 6.2. Thus, of the four hemoglobins, A has the highest net positive charge and J, I, and H follow in order.

The electrophoretic studies showed, in addition to the mobility differences, that the carriers of hemoglobin J possessed more of the abnormal hemoglobin than hemoglobin A. This result may be discerned in the paper electrophoresis experiments shown in Fig. 1. The proportions were found to be 40 percent A and 60 percent J by moving-boundary electrophoresis at *p*H 6.5. The other asymptomatic carrier states for the abnormal hemoglobins are characterized by the presence of a preponderance of hemoglobin A (*1*).

The solubility as amorphous ferrohemoglobin of one of the AJ samples was determined with use of the standard-

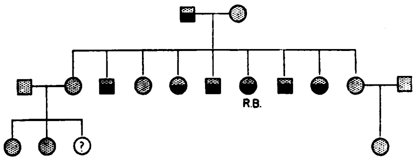

Fig. 2. Incidence of hemoglobin in the R.B. family under study. Hemoglobin J is indicated by black, and normal hemoglobin by gray.