Reports

Reaction of Hydrogen with Oxygen Adsorbed on a Platinum Catalyst

Abstract. *The release of hydrogen atoms by a platinum surface in contact with molecular hydrogen occurs if there is oxygen in the system. In particular, it is sufficient that the oxygen be adsorbed at the surface of the metal.*

Khoobiar has reported recently (*1*) that tungsten oxide, WO_3, could be turned blue by passing hydrogen at room temperature over the oxide mixed with a catalyst consisting of platinum supported on alumina. Although hydrogen atoms are known to react with WO_3 to form tungsten blue (*2*), the origin of the hydrogen atoms in the experiment of Khoobiar is not clear.

One possibility is that hydrogen atoms leave the platinum surface of the catalyst. Such an explanation was rejected by Taylor (*3*) in a critical survey of work done in the twenties which resembles the work of Khoobiar in many respects. Taylor concluded that oxygen was essential to the release of hydrogen atoms by a platinum surface. He proposed a reaction between adsorbed oxygen atoms O_a and molecular hydrogen to yield adsorbed hydroxyl $(OH)_a$ and free hydrogen atoms:

$$O_a + H_2 \rightarrow (OH)_a + H \nearrow \qquad (1)$$

This may be followed by:

$$(OH)_a + H_2 \rightarrow H_2O + H \nearrow \qquad (2)$$

The work of Martin and Rummel (*4*) supports Taylor's conclusions. Using a mass-spectrograph, they looked in vain for hydrogen atoms on the vacuum side of a palladium membrane through which H_2 was diffusing. Yet, they were able to detect other free radicals leaving the surface after reaction with adsorbed hydrogen. These results prompt us to publish some very simple experiments designed to elucidate the experiment of Khoobiar.

First, as postulated by Taylor, oxygen appears to be a necessary coreactant in this experiment. To show how oxygen participates in the reaction, we made a glass reaction tube (100 cm^3 capacity) with stopcocks at both ends, 40 cm apart. At one end, we placed 50 mg of platinum-alumina catalyst similar to that used by Khoobiar (*5*). At the other end, we placed 50 mg of WO_3 prepared by heating at 300°C tungstic acid reagent powder (from Matheson, Coleman and Bell). The catalyst was then reduced for 2 hours at 360°C in hydrogen flowing directly from the tank, while the tungsten oxide remained at room temperature. The stopcocks were then closed, and the tube was cooled to room temperature. The catalyst and tungsten oxide were then mixed by shaking the reaction tube, and the mixture was allowed to stand in hydrogen for about 72 hours. No visible reaction occurred. Now a second stopcock was sealed onto one of the others, creating an interspace or "doser" 1.4 cm^3 in volume. Over the course of several hours, five doses of air were allowed to diffuse into the hydrogen in the tube. One could see the tungsten oxide layer gradually turn blue from the top down as the air diffused into it (*6*).

Second, the blue reaction is immediate and reversible at room temperature. If one places a mixture of well-reduced catalyst and tungsten oxide in a thin layer at the bottom of a long tube (½ cm in diameter), and then passes hydrogen over it (flow rate, 50 cm^3/min), one can watch the advancing blue front in the tungsten oxide as hydrogen replaces the air. After the hydrogen flow is stopped, the mixture will revert to its original grayish yellow color as the air diffuses back.

Third, although oxygen is necessary for the blue reaction, oxygen adsorbed on the catalyst is quite sufficient to cause it. To demonstrate this, a sample of catalyst was reduced in hydrogen, then exposed to the air and mixed with the WO_3 powder. A sample (0.1 g) of the mixture was placed in a glass tube and a stream of nitrogen (80 cm^3/min) was passed over it for 15 minutes. Then a stream of hydrogen (25 cm^3/min) was added to the nitrogen stream. The powder was thoroughly blue in half a minute. After this time, the hydrogen flow was shut off and the nitrogen flow was continued for 25 minutes. Since no visible bleaching of the blue color occurred during this time, we assume that the blue reaction was due to adsorbed oxygen and not to impurities in the gas stream which somehow escaped a gas purifier consisting of a sample of reduced platinum catalyst. We conclude that reactions of adsorbed oxygen will explain the experiment of Khoobiar.

It must be noted that the reaction:

$$O_a + H_2 \rightarrow H_2O \qquad (3)$$

has been studied calorimetrically (*7*). The heat released is 42 kcal/mole. Therefore, since the dissociation energy of H_2 is 104.2 kcal, the following reaction is endothermic to the extent of only $(104/2) - 42 = 10$ kcal:

$$O_a + \frac{3}{2}H_2 \rightarrow H_2O + H \nearrow \qquad (4)$$

While the release of hydrogen atoms does not, of course, occur directly by the overall reaction depicted in Eq. 4, the thermodynamic argument helps in understanding why the production of hydrogen atoms is only slightly endothermic and therefore possible at room temperature. In other words, the thermodynamically unfavorable release of hydrogen atoms is coupled (*8*) to the thermodynamically favorable formation of water.

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References and Notes

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2. H. W. Melville and J. C. Robb, *Proc. Roy. Soc. London Ser A* **196**, 445 (1949).
3. H. S. Taylor, *Chem. Rev.* **9**, 1 (1931).
4. T. W. Martin and R. E. Rummel, *Science* **143**, 797 (1964).
5. We thank Dr. J. Sinfelt (Esso Research and Engineering Company) for sending us samples of catalyst similar to those used by Khoobiar.

6. A much more dramatic demonstration can be done by snapping one of the stopcocks, and watching the tungsten oxide turn blue during the resultant explosion. However the heat generated by the hydrogen-oxygen reaction might be an interfering factor.
7. H. Chon, R. A. Fisher, E. Tomeszko, J. G. Alston, *Actes 2e Congr. Intern. Catalyse Paris*, 1960 (Technip, Paris, 1960), vol. 1, p. 217.
8. I. Prigogine and R. Defay, *Chemical Thermodynamics*, D. H. Everett, trans. (Longmans, London, 1954), p. 42.
9. This work was carried out while one of us (H.W.K.) was on a leave from Oak Ridge National Laboratory. Partial support by NSF grant GP 2305 is gratefully acknowledged.

30 March 1964

Flowage Differentiation

Abstract. *Flowage differentiation is an experimentally demonstrable process capable of causing crystal and chemical fractionation in nature. It is a mechanism for forming olivine-rich rocks in a vertical or steeply dipping position without prior concentration on a flat floor. It explains the field observation that the chilled margin of a mafic intrusion may not be a representative sample of the average composition of the parent magma. In contrast to previous hypotheses of origin for composite dikes, it causes fractionation during and as a result of a single movement of magma rather than by multiple injections.*

The concept of flowage differentiation in the form described in this report is new to petrologic thought. In a flowing magma with solid and fluid phases, the solids can segregate to form mineral accumulates because of the inherent flow properties of the mixture. Segregation takes place away from the walls and toward the central axis of a conduit. The mechanism may be one of the processes which cause magmas to separate into diverse rock types and, in certain circumstances, may be more important than gravity, convection currents, or other processes in forming monomineralic concentrations. In addition to mechanical concentration of minerals, the process may produce chemical or cryptic zoning among the minerals themselves. Thus, early-formed olivine with a higher Mg/Fe ratio may be concentrated closer to the conduit axis than later-formed olivine with a lower Mg/Fe ratio. The feeder dike to the Muskox Intrusion which we describe here is a geological example. The picritic dikes of Skye (Bowen's "peridotite" dikes) recently described by Drever and Johnston (*1*) exhibit similar features. The process may also explain concentric zoning in ultramafic-gabbro intrusions.

The Muskox Intrusion is a Precambrian (1175 million years) layered ultramafic-mafic pluton situated in the Northwest Territories of Canada, crossing the Arctic Circle near 115°W longitude (*2*). It crops out for 74 miles (119 km) along a northwesterly trend. In cross-section the intrusion consists of a feeder dike connected to an overlying funnel-shaped body (Fig. 1). The latter part contains gently dipping layers of dunite, peridotite, pyroxenite, gabbro, and granophyre. In this report we discuss the feeder dike alone.

The feeder dike crops out for 37 miles, and ranges from 150 m to 550 m in width. It is nearly vertical and has sharply defined, chilled contacts with the surrounding Precambrian rocks (1765 million years and older). At its northern end it is connected to, and plunges under, the main body of the intrusion.

There are two types of rock, picrite (olivine-rich) and norite (olivine-poor, hypersthene gabbro), forming vertical zones parallel to the walls of the dike. Picrite may be considered as a norite plus 20 to 40 percent olivine. The margins of the dike are always formed of norite, while picrite is confined to the central third; picrite forms discontinuous lenses which are more continuous nearer the main body of the intrusion. In this latter area a third norite zone divides the medial picrite into two parts. Contacts between norite and picrite are sharp to transitional within a meter.

Mineralogical zoning in the dike has been described by Zwartkruis and Smith (*3*). The principal minerals are olivine (Fo_{59}-Fo_{78}), orthopyroxene (En_{67}-En_{82}), clinopyroxene ($Mg_{36}Fe_{24}Ca_{40}$-$Mg_{46}Fe_{14}Ca_{40}$), and plagioclase (An_{45}-An_{85}). The minerals indicate symmetrical zoning in the dike in the following ways. (i) Olivine increases in grain size, abundance, and Mg/Fe ratio from the dike margins toward the center. (ii) Plagioclase decreases in abundance, and increases in grain size, An-content, and degree of order from the margins toward the center. (iii) Pyroxenes increase in Mg/Fe toward the center.

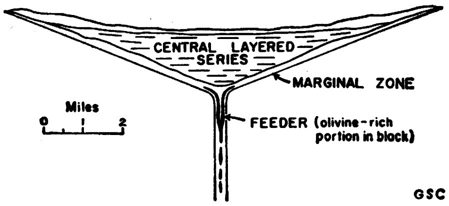

Fig. 1. Generalized section across Muskox Intrusion showing location of feeder dike and position of olivine-rich (picrite) zones within it.

There are three features of the dike indicative of its mode of origin. First, it is zoned parallel to vertical walls. Thus an origin by gravitative differentiation does not apply. Secondly, there are no chilled contacts between zones, only against the country rocks. Thus, an origin by successive injection of magmas of notably different age does not apply. Thirdly, there is a mineralogical symmetry to the rocks of the feeder which precludes random injection of separate norite and picrite magmas, even at high temperatures. The problem, then, is to explain how the first-crystallized, high-temperature minerals (such as olivine) in a magma can occur in the center of a vertical conduit, in the last part solidified completely, rather than along the conduit walls. In view of the inadequacy of current geological hypotheses, we devised experiments to test the possibility that the process responsible is analogous to flow phenomena observed in the transport of solid-fluid mixtures in certain industrial processes. Concentration of solid fractions toward

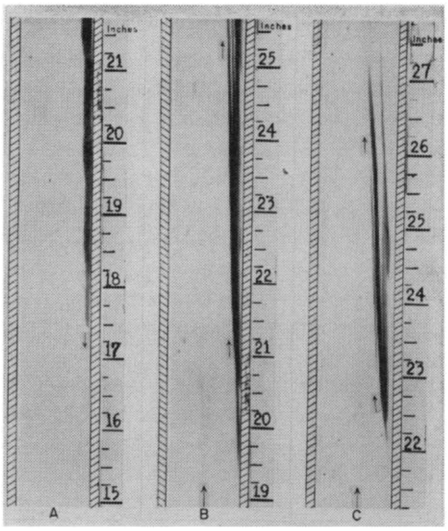

Fig. 2. Inward displacement of solid particles during vertical flow of fluid in a rectangular lucite conduit. The solid particles are Paraplex plastic, 0.053 to 0.037 mm in size, and the fluid is Shell motor oil SAE 20. Downward movement of solids in oil along margin of conduit is shown in *A*. Incipient inward displacement of solids as oil is forced up the conduit from below is shown in *B*. Continued migration of solids into central axis of conduit is shown in *C*. Average fluid velocity is 2 cm sec^{-1}.