KINETICS AND MECHANISM OF THE ANATASE/RUTILE TRANSFORMATION, AS CATALYZED BY FERRIC OXIDE AND REDUCING CONDITIONS

EMERSON F. HEALD,[1] *Department of Chemistry*
Victoria University of Wellington
Wellington, New Zealand

AND

CLAIR W. WEISS, *Department of Chemistry, Thiel College*
Greenville, Pennsylvania 16125

ABSTRACT

Traces of ferric oxide have a strong catalytic effect on both nucleation and growth phases of the transformation of TiO_2 from anatase to rutile. This effect is greatly enhanced in atmospheres of low f_{O_2}. Using X-ray diffraction techniques, the kinetics of the phase transformation were studied at 1 atm. and 900 to 1000°C, for anatase mixed intimately with up to 0.2% by weight hematite (Fe_2O_3) in CO_2/H_2 atmospheres holding f_{O_2} between 10^{-10} and 10^{-17} atm. The rate data fit the contracting reaction interface equation, $d\alpha/dt = k(1 - \alpha)^{1/3}$, where α is the extent of reaction. The rate constant k is given by: $k = W_{Fe_2O_3}^2 (k'f_{H_2} + k''f_{CO} + k'' ')$, where k', k'', and $k'' '$ are constants. These results are consistent with a mechanism in which the phase transformation begins at nuclei formed at the surfaces of anatase particles coated with a thin layer of hematite. In view of the concerted movement of Ti^{4+} and O^{2-} ions involved in the transformation (Shannon and Pask, 1964), the nuclei must be anion vacancies (AV). The number of AV formed in hematite and transferred to anatase, and thus the number of reacting chains in the growth phase of the reaction (*e. g.*, the rate) are controlled by reactions of the type:

$$2 O^{2-}(h) + H_2(g) \rightarrow 2 OH^-(h) + 2 e^- (h) \quad \text{(slow)}$$

$$2 OH^-(h) \rightarrow O^{2-}(h) + AV(h) + H_2O(g) \quad \text{(fast)}$$

It is assumed that not enough hematite is present to completely coat the anatase particles, and in fact it turns out that at high $W_{Fe_2O_3}$ the rate is independent of $W_{Fe_2O_3}$.

INTRODUCTION

Three crystalline forms of titanium dioxide are known to occur naturally, and a fourth has recently been prepared artificially at high pressures and temperatures. One form, brookite, has not yet been prepared in the laboratory. Most commercial processes, usually involving precipitation from chloride or sulfate solutions, result in anatase, whereas many applications require rutile. The apparently

[1] Present Address: Department of Chemistry, Thiel College, Greenville, Pennsylvania 16125.

irreversible transformation of anatase into rutile is therefore of some interest to such diverse industries as paint manufacturing, ceramics, and electronics, as well as to mineralogists.

The transformation occurs at temperatures ranging from $600°C$ to $1100°C$, depending chiefly on the impurities present in the anatase. Some, such as Cu^{2+}, Co^{2+}, Fe^{2+}, etc., are known to accelerate the reaction; others, such as SO_4^{2-}, PO_4^{3-}, etc., retard it. A review of the effects of impurities has been given by Shannon (1964).

Both anatase and rutile crystallize in the tetragonal system. Rutile has an oxygen lattice which is nearly hexagonally close packed, and anatase one which is nearly cubic close packed. In both structures, Ti^{4+} is present as TiO_6 octahedra which share edges and corners. Because of the requirement of electroneutrality, there are an equal number of empty oxygen octahedra. In rutile there are straight chains of octahedra; in anatase zig-zag chains.

It is evident from the differences in the structures and the high activation energy (100 kcal/mole or more, depending on conditions) that a substantial rearrangement of the structure must occur during the transformation. Shannon and Pask (1964) have found on reacting single crystals of anatase that a preferred orientation of the product rutile crystals occurs, but with no preservation of the anatase axes of symmetry. They have proposed a mechanism in which the (112) nearly close-packed oxygen planes of anatase are retained as the (100) nearly close-packed oxygen planes of rutile. Within these planes, a cooperative rearrangement of Ti^{4+} and O^{2-} ions is thought to occur in which the Ti^{4+} ions need break only two of their six Ti-O bonds in order to reach their new sites.

There have been a number of kinetic studies. Using spectroscopically pure anatase, Czanderna, Rao, and Honig (1957) found the transition fit "second order kinetics," in which a plot of $1/(1 - \alpha)$ is linear, where α is the extent of reaction. Rao (1961) later reexamined their results in the light of more accurate analyses and concluded that the reaction was "first order," in which a plot of $\log(1 - \alpha)$ vs. time is linear. No induction period was found in their work.

Quite a different situation arises in commercially prepared powders. Shannon and Pask (1965) invariably observed an induction period, up to $\alpha = 0.3$, in which the nucleation rate predominates, followed by a stage in which growth predominates. The results is a sigmoid curve when α is plotted against time. The nucleation stage was found to fit the equation:

$$\log \alpha = kt + \text{constant},$$

which is based upon the assumption of one-dimensional, linear, branching nuclei and a constant growth rate. The growth, or deceleratory, stage fit at least three rate laws equally well. These were:

$$(1 - \alpha)^{1/3} = kt + \text{constant} \tag{1}$$

based upon the model of a reaction interface occurring as a contracting sphere or cube ("phase boundary equation");

$$\log (1 - \alpha) = kt + \text{constant} \tag{2}$$

based upon random nucelation and rapid growth; and

$$[\log (1 - \alpha)]^{1/3} = kt + \text{constant} \tag{3}$$

in which overlapping of nuclei is taken into account.

Shannon and Pask (1965) also studied the anatase/rutile transformation in the presence of 1 percent CuO and in hydrogen/nitrogen atmospheres. Both accelerated the reaction. They concluded that impurities or conditions which increase the number of oxygen vacancies accelerate the reaction, and those which form interstitial ions slow it down. The hydrogen would reduce some Ti^{4+} to Ti^{3+}, a process which introduces some anion vacancies in order to maintain electroneutrality. Substitution of divalent ions such as Cu^{2+} would also introduce anion vacancies, for the same reason. Introduction of ions such as S^{6+} or P^{5+} would require interstitial oxygen ions for electroneutrality. They would be expected to get in the way of the reaction, and to slow it down.

<center>EXPERIMENTAL</center>

The materials used were "Baker Analyzed" reagent grade titanium dioxide, lot no. 31310, and "Baker Analyzed" reagent ferric oxide, lot no. 31325. According to the label, the impurities present in the titanium dioxide (referred to in what follows as "pure" anatase) were 0.01 percent water soluble salts, 0.0002 percent arsenic, 0.002 percent iron, 0.0045 percent lead, and 0.01 percent zinc. After weighing, samples were mixed by grinding manually in an agate mortar (Victoria University), or automatically in a "Wig-L-Bug" apparatus (Thiel College).

The temperature in the hot zone of a vertical-tube, platinum-wound furnace was controlled to $\pm 3°C$ by a Leeds and Northrup Electromax controller activated by a platinum/platinum-10 percent rhodium thermocouple. A second thermocouple, calibrated against the melting points of gold (1063°C) and diopside (1392°C), was used to measure the temperature.

A gas mixer of the type described by Darken and Gurry (1945) was used to prepare accurately known mixtures of hydrogen and carbon dioxide (and in some cases carbon monoxide and carbon dioxide), which were passed upward over the sample in the furnace tube. Gas compositions were accurate to ± 2 percent. The entire apparatus was checked by determining the CO_2/H_2 ratio (and thus the fugacity of oxygen) at the iron/wüstite equilibrium, and comparing it against the results of Darken and Gurry.

Samples were hung in the furnace tube in small platinum envelopes suspended

from fine platinum wires. The total mass of sample, envelope, and wires was less than 0.01 g., minimizing the time for the sample to reach furnace temperature. Quenching was accomplished by drawing the sample out into the air.

Analysis for anatase and rutile was carried out by measuring the relative intensities of the two strongest peaks in their X-ray powder diffraction patterns (Spurr and Myers, 1957). Calibration of the diffractometers, a Philips instrument (Victoria University) and a venerable Norelco (Thiel College), both equipped with goniometers, Geiger counters, and strip chart recorders, was accomplished with known mixtures of anatase and rutile. In order to minimize the amount of sample needed, the sample powders were spread evenly on glass slides for analysis. Results on standard samples run on the two different instruments showed a precision of ±2 percent. Because the unknown samples were run under the same conditions as the standards, it is thought that the accuracy of the analyses is also in the range ±2 percent.

Results

In Figure 1 are shown some typical kinetic curves for the conversion of anatase into rutile at 1000°C. The curve following the black squares is that of "pure" anatase in air. It is essentially the same as that obtained by Shannon and Pask (1965) for similar materials. There is an induction or nucleation period, followed by a growth period, giving rise to a sigmoid curve.

Addition of 0.087 percent hematite, Fe_2O_3, (black circles) to the anatase speeds up the growth phase of the reaction, but has little effect on the nucleation period. Placing the pure anatase powder in a slightly reducing atmosphere ($CO_2/H_2 = 27.4$, $\log f_{O_2} = -11.20$) (open squares) shortens the nucleation period but has little effect on the rate of growth. However, a dramatic change in the reaction is obtained when both the reducing atmosphere and 0.087 percent hematite are used (open circles): The nucleation period is nearly eliminated, and the rate of growth greatly accelerated. The result is a half life of some 17 minutes compared to 154 minutes for pure anatase in air, a nine-fold decrease.

Typically, the presence of hematite together with the use of a reducing atmosphere greatly shortened or altogether eliminated the induction period. In almost all experiments it was possible to get a satisfactory fit of data at all values of α (except those near unity) to a single kinetic equation. Both the phase boundary equation (1) and the random nucleation equation (2) gave good results, as shown in Figures 2 and 3. In most cases the phase boundary equation fit the data to slightly higher values of α than did the random nucleation equation. For that reason, the phase boundary equation is used in all further treatment of data. Essentially the same results are obtained with the random nucleation equation.

HEALD AND WEISS
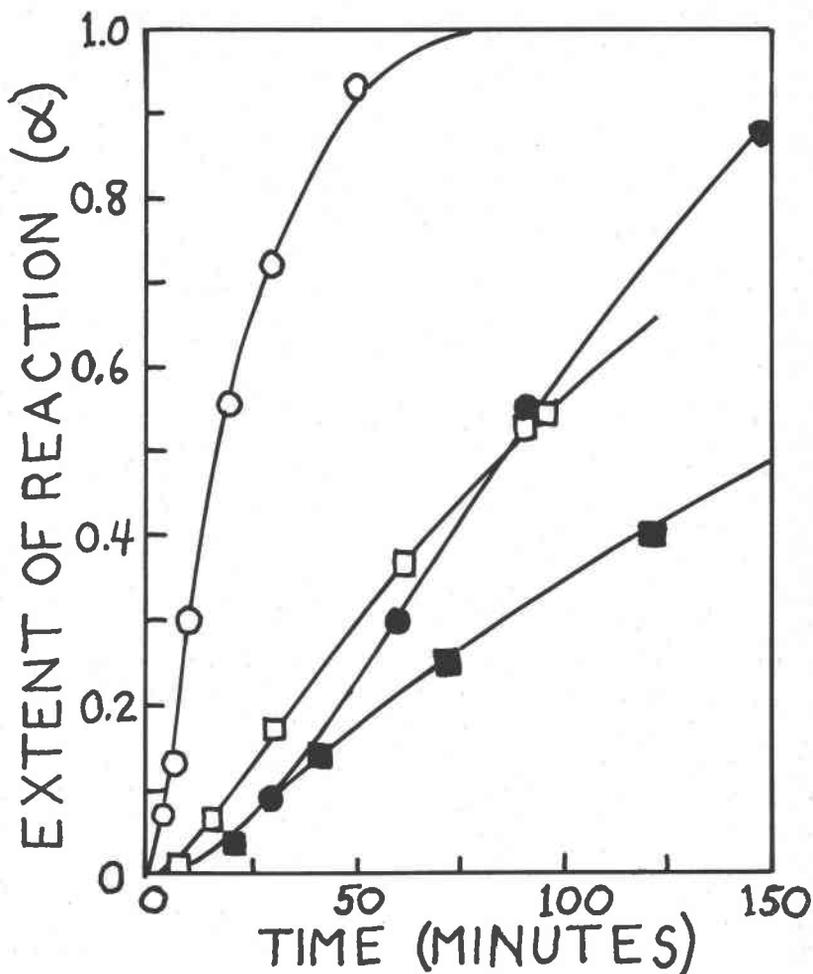
F<small>IG</small>. 1. Extent of reaction (α) of the anatase/rutile transformation at 1000°C and 1 atm. Solid squares represent "pure" anatase in air; solid circles anatase plus 0.087% hematite in air; open squares "pure" anatase in $CO_2/H_2 = 27.4$; open circles anatase plus 0.087% hematite in $CO_2/H_2 = 27.4$.

A satisfactory fit to the data could not be obtained with the over-lapping nuclei equation (3), or with various other equations used in solid-state kinetics.

A number of other oxides were tried, to see whether hematite is unique in its effect on the transformation. The results are summarized in Table 1. Two oxides, tenorite (CuO) and magnetite (Fe_3O_4), were found to have a strong effect on the rate constant, whereas wüstite

(FeO) and zincite (ZnO) did not. The essential difference between these two groups of oxides is that under the conditions of the experiments those in the first group can be reduced to a lower oxide, while those in the second group cannot. It appears that loss of oxygen to form a lower oxide (but not the metal) in an oxide in contact with anatase is what is effective in catalyzing the transformation.

Why hematite is the most effective became evident on examining the mixtures under the microscope. Mixtures of anatase with hematite appeared uniformly pink, as if the more finely divided particles of hematite were spread more or less evenly on the larger anatase particles. This was not true of mixtures of anatase with the other oxides. Rather, the oxide (when it could be distinguished by color) appeared as discrete particles scattered throughout the matrix of anatase particles. The resulting lack of interphase contact would therefore have made these oxides less efficient than hematite. It appears that comparisons of the effectiveness of different oxides as catalysts are quantitatively meaningful only if the particle sizes and degree of mixing can be made the same.

An estimate of the energy of activation E_a of the Fe_2O_3-catalyzed transformation under reducing conditions can be made by plotting log
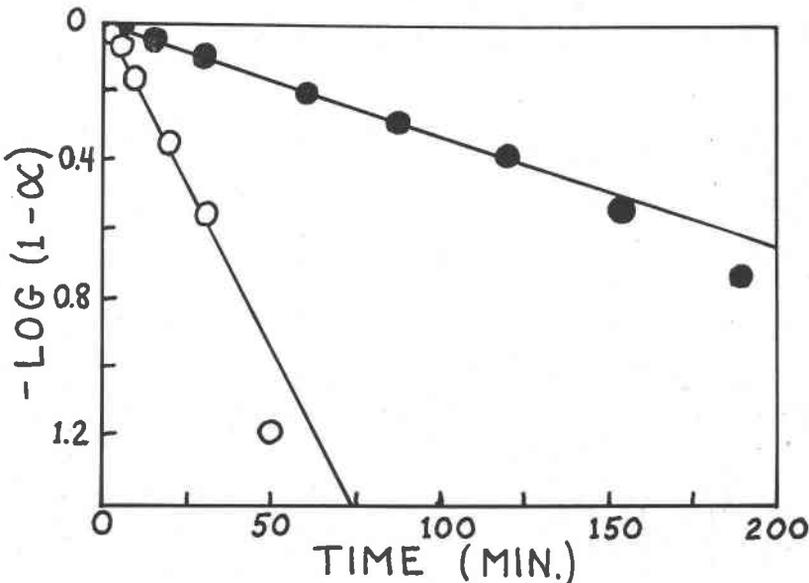
Fig. 2. Random nucleation equation plot, anatase/rutile transformation in the presence of 0.087% hematite at 1 atm. Open circles represent 1000°C and $CO_2/H_2 = 27.4$; solid circles 945°C and $CO_2/H_2 = 2.75$.
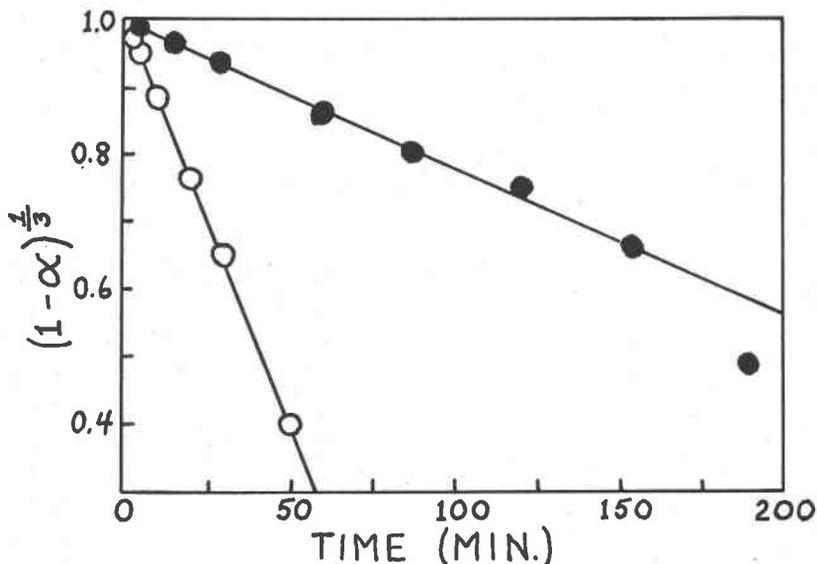
FIG. 3. Phase boundary equation plot, anatase/rutile transformation in the presence of 0.087% hematite at 1 atm. Open circles represent 1000°C and CO_2/H_2 = 27.4; solid circles 945°C and CO_2/H_2 = 2.75.

Table 1. Comparison of Effectiveness of Oxides in Catalyzing the Anatase/ Rutile Transformation at 1000°C and CO_2/H_2 = 2.75 (log f_{O_2} = -13.40).

Oxide	Weight Percent	Rate Constant	Relative Rate*
Fe_2O_3	0.0294	0.00768 min.$^{-1}$	87.5
CuO	0.075	0.00534	23.9
Fe_3O_4	0.22	0.00723	11.0
FeO	1.13	0.01302	2.04
ZnO	0.85	0.00452	1.77

*This quantity is the rate constant divided by the percentage of oxide and by the rate constant for pure anatase, 0.00298 min.$^{-1}$

k vs. $1/T$; according to the Arrhenius equation, the slope of the plot is $-E_a/2.3R$. Figure 4 is such a plot, for 0.100 percent Fe_2O_3 plus anatase, and $CO_2/H_2 = 2.49$. A least-squares determination of the slope gives an activation energy of 124 ± 16 kcal/mole. This value compares well with that given by Shannon and Pask (1965) for Baker and Adamson reagent grade anatase, 100 kcal/mole. It is also in accord with their observation that the presence of an impurity oxide increases the activation energy even though reaction can occur at a lower temperature. They attribute this somewhat anomalous situation either to the extra energy required for foreign ions to diffuse into the anatase lattice, or to compound formation.

Experiments were done to determine the order of the transformation with respect to ferric oxide and the gas composition. Experimental results for mixtures of ferric oxide and anatase at 946°C and $CO_2/H_2 = 2.49$ (log $f_{O_2} = -14.43$) are shown in Figure 5. The log of the rate constant k of the phase boundary equation (1) is plotted against the log of the weight fraction of ferric oxide, $W_{Fe_2O_3}$. For the three most
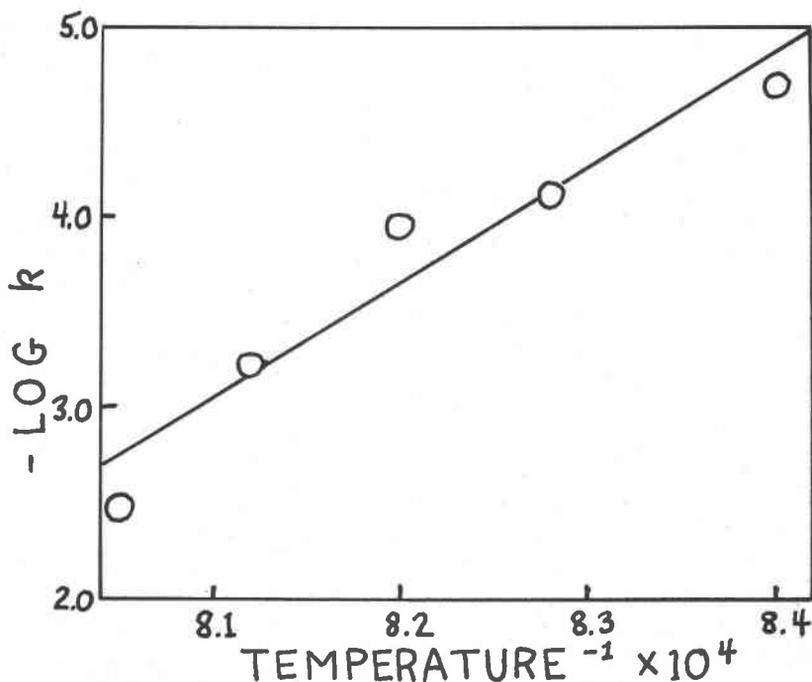
FIG. 4. Arrhenius plot, anatase/rutile transformation in the presence of 0.100% hematite. Pressure = 1 atm.; $CO_2/H_2 = 2.49$. Rate constant k is from the phase boundary equation. The units of k are min.$^{-1}$, and of temperature are °K.

"dilute" mixtures, reaction in anatase itself was significant, and had to be corrected for. The uncorrected rate constants appear as open circles, the corrected values as black circles. The slope of the plot is the order in ferric oxide; a least squares analysis of the data gives the value 2.42 ± 0.20. The reaction is therefore assumed to be second order in ferric oxide.

On the grounds that anion vacancies are related to oxygen fugacity, an attempt was made to determine the order of the transformation with respect to oxygen. In Figure 6, for 0.0294 percent hematite and anatase at 1000°C, the log of the rate constant is clearly not a linear function of log f_{O_2}, so the reaction does not have a simple order with respect to oxygen. Similar results were obtained for 0.087 and 0.165 percent hematite mixtures at 945°C.

This makes sense, because f_{O_2} is really only a convenient measure of the reducing capacity of the atmosphere; at oxygen fugacities in the range of 10^{-10} to 10^{-17} atm., there is not enough oxygen present to
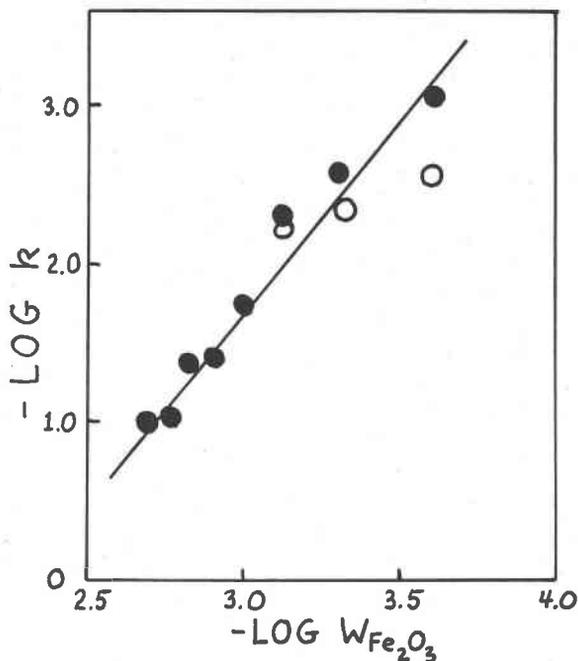
FIG. 5. Effect of the weight fraction of hematite ($W_{Fe_2O_3}$) on the anatase/rutile transformation at 946°C and 1 atm. $CO_2/H_2 = 2.49$. Rate constant k is from the phase boundary equation; its units are min.$^{-1}$ Points represented by black circles have been corrected for the reaction in pure anatase; those represented by open circles have not.
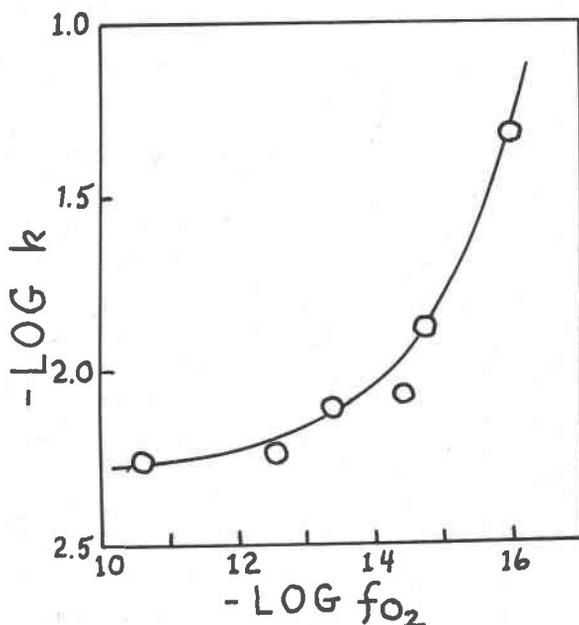
F<small>IG.</small> 6. Effect of reducing atmosphere, as expressed by oxygen fugacity, on the anatase/rutile transformation in the presence of 0.0294% hematite at 1000°C and 1 atm. Rate constant k is from the phase boundary equation; its units are min.$^{-1}$

have much effect on the reaction. The reducing agent is clearly hydrogen (as well as carbon monoxide, from the water gas equilibrium). A plot was made of the log of the fugacity of hydrogen ($\log f_{H_2}^0$) in the mixture of gasses fed into the furnace. This plot was also not linear, for all three compositions noted above.

The reason the transformation does not appear to follow a simple order in gas composition is evident from Figure 7. Here the rate constant k itself is plotted against $f_{H_2}^0$. In the range $0 < f_{H_2}^0 < 0.7$ atm., the experimental points fall close to a straight line whose equation is

$$k = A f_{H_2}^0 + B \qquad (4)$$

where A and B are constants. Similar results were again obtained for the 0.087 and 0.165 percent Fe_2O_3 mixtures at 945°C.

A reaction involving CO is required by the water gas equilibrium:

$$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g) \qquad (5)$$
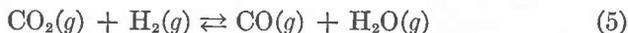
Thus the hydrogen initially present in the gas mixture (indicated by $f_{H_2}^0$ in Equation (4)) becomes converted to a mixture of H_2 and CO, such that (assuming ideal gas behavior):

$$f_{H_2}^0 = f_{H_2} + f_{CO}$$
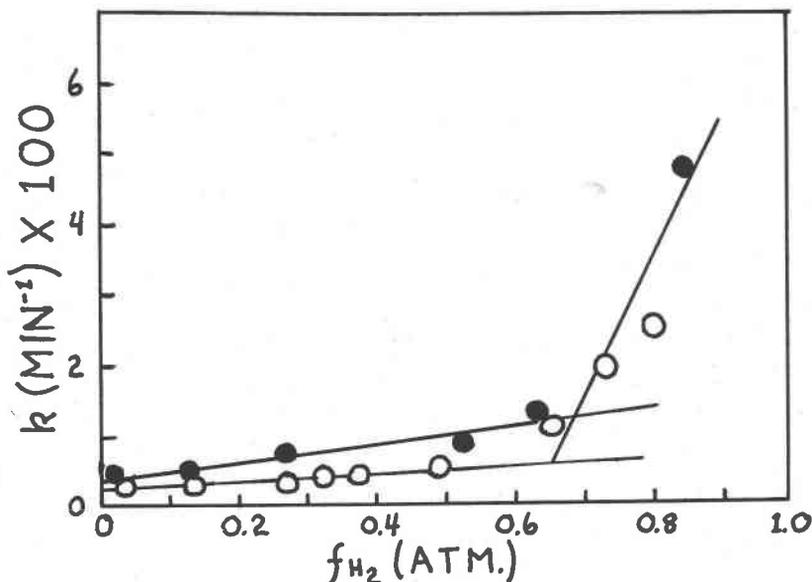
Fɪɢ. 7. Effect of hydrogen fugacity in CO_2/H_2 atmospheres on the anatase/rutile transformation at 1000°C and 1 atm. Solid circles represent anatase plus 0.0294% hematite; open circles "pure" anatase.

This is true because of the stoichiometry of Equation (5) and the lack of any significant side reactions.

Some experiments have been done in CO_2/CO mixtures, and the data found to fit the equation $k = A'f_{CO} + B'$ for mixtures containing 0.125 percent Fe_2O_3 at 946°C. It would appear that CO behaves in much the same way as H_2 in the transformation.

It is informative to compare these results with those obtained with pure anatase (open circles, Figure 7). This comparison could conveniently be made only at 1000°C, because of the slowness of the pure anatase reaction at 945°C. A similar linear relationship is obtained for pure anatase, holding for $f_{H_2}^0$ below about 0.7 atm. At $f_{H_2}^0$ above 0.7 atm, the reaction is much faster than Equation (4) predicts, for both pure anatase and for mixtures of anatase and Fe_2O_3.

These results are consistent with the following statements:

(1) At $f_{H_2}^0$ less than about 0.7 atm, nucleation of the anatase/rutile transformation occurs by essentially the same process, whether or not hematite is present. This process could very well be the formation of anion vacancies in the anatase phase.

(2) At $f_{H_2}^0$ greater than about 0.7 atm, a different mechanism occurs,

which is also independent of the presence of hematite. This could involve a general breaking up of the anatase lattice, as significant amounts of Ti^{4+} are reduced to Ti^{3+}.

DISCUSSION

For CO_2/H_2 atmospheres in the range $0 < f_{H_2}{}^0 < 0.7$ atm, the rate constant for the ferric oxide-catalyzed anatase/rutile transformation can be summarized as:

$$k = W_{Fe_2O_3}{}^2(k'f_{H_2} + k''f_{CO} + k''') \qquad (6)$$

A satisfactory mechanism involves (1) formation of anion vacancies in the ferric oxide as a rate-determining step, (2) transfer of the anion vacancies to the anatase, and (3) nucleation by the anion vacancies of the phase transformation. Each of these steps will be considered in detail:

(1) Anion vacancies can be produced in the hematite phase by at least three different processes. The following reactions apply in the case of hydrogen:

$$2\ O^{2-}(h) + H_2(g) \rightarrow 2\ OH^-(h) + 2\ e^-(h)\ \text{(slow)} \qquad (7a)$$

$$2\ OH^-(h) \rightarrow O^{2-}(h) + AV(h) + H_2O(g)\ \text{(fast)} \qquad (7b)$$
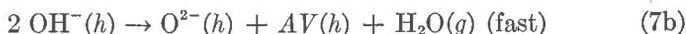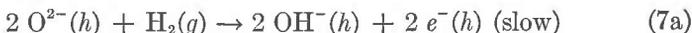
Here (h) refers to the hematite phase, and (g) to the gas phase. The net rate of these steps is:

$$d[AV]/dt = k[O^{2-}]_h{}^2 f_{H_2}$$

where $[O^{2-}]_h$ is the concentration of oxide ions from hematite in the entire sample, hematite plus anatase. This quantity will be proportional to $W_{Fe_2O_3}$, assuming intimate contact between the two phases.

Similar reactions involving CO are:

$$CO(g) + 2\ O^{2-}(h) \rightarrow CO_3{}^{2-}(h) + 2e^-(h) \qquad \text{(slow)} \qquad (8a)$$

$$CO_3{}^{2-}(h) \rightarrow O^{2-}(h) + AV(h) + CO_2(g) \qquad \text{(fast)} \qquad (8b)$$
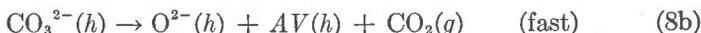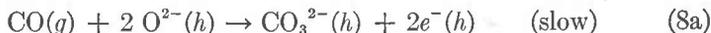
The hematite may also decompose by itself, forming oxygen gas:

$$2\ O^{2-}(h) \rightarrow O_2(g) + 2\ AV(h) + 4e^-(h) \qquad (9)$$
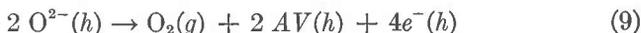
Reactions (7), (8), and (9) appear to take place at comparable rates, giving rise to the overall rate constant of Equation (6).

(2) Since the hematite occurs as a finely-divided coating on the surfaces of larger anatase particles, diffusion of an oxide ion from the hematite to the anatase is possible. This corresponds to the transfer of the anion vacancy from the hematite to the anatase. Such a transfer

appears to be faster than reactions which would destroy anion vacancies, such as combination of the electrons formed in (7), (8), and (9) with Fe^{3+} to form Fe^{2+}, followed by rearrangement of the hematite structure to form magnetite.

(3) Once in the anatase phase, the anion vacancy could nucleate the anatase/rutile transformation, as suggested by Shannon and Pask (1964, 1965). Since diffusion of anion vacancies into the bulk of the anatase lattice would be slow, nucleation would be limited to the surfaces of the anatase particles. One would then expect that the reaction would grow inward from the surface, and that the phase boundary equation (1) would apply.

As long as the surfaces of the anatase particles are not completely covered with hematite, the second order dependence on ferric oxide should be valid. The number of nuclei formed, and thus the number of growing chains (e. g., the rate) should depend on the amount of ferric oxide present. Furthermore, if enough ferric oxide were present, the surfaces of the anatase particles should get "saturated" with it, and no further addition of ferric oxide would make any difference. As shown in Figure 8, this appears to be the case. The rate of the reac-
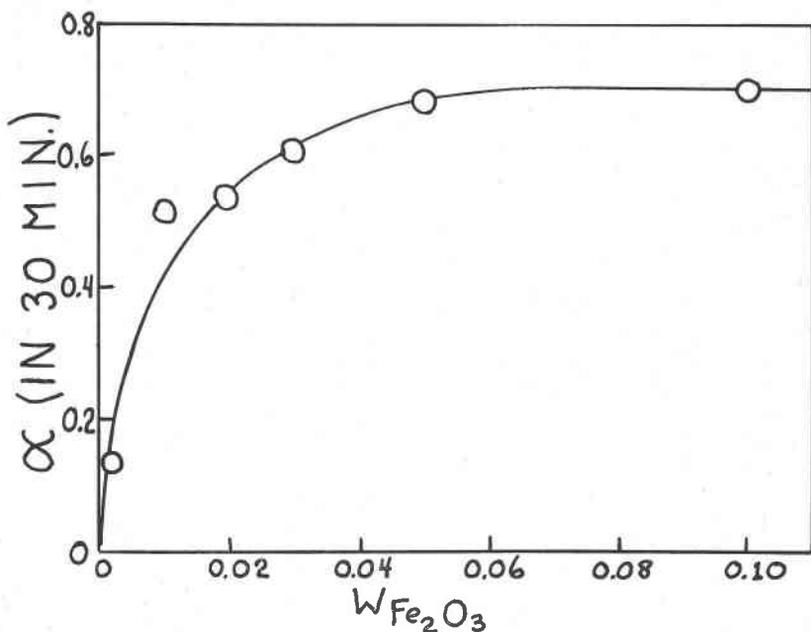
FIG. 8.   Effect of high $W_{Fe_2O_3}$ on the anatase/rutile transformation at 854°C and 1 atm $CO_2/H_2 = 2.49$.

tion appears to level off between 2 and 5 percent Fe_2O_3. This corresponds roughly, as noted by Shannon and Pask (1965), to the amount of ferric oxide needed for the formation of a monomolecular layer on the anatase particles.

One may also ask what happens to the ferric ions. Presumably they are reduced to ferrous ions, which then enter the anatase lattice by diffusion, creating more anion vacancies and further accelerating the reaction. No direct experimental evidence for the formation of a new phase is available. All that can be said is that the uniform pink color of the hematite-coated anatase fades to white after about five minutes at temperature in a reducing atmosphere.

The rate-controlling step of the reaction in pure anatase is probably similar to reactions (7), (8), and (9), except that the anion vacancies are formed directly in the anatase phase. Again, it would be expected that the reactions would take place chiefly on the surfaces of the anatase particles, and that the phase boundary rate equation (1) would represent the data well. The reaction in pure anatase would become significant only if the amount of hematite present were small.

References

CZANDERNA, A. W., C. N. R. RAO, AND J. M. HONIG (1957) The anatase-rutile transition I. Kinetics of the transformation of pure anatase. *Trans. Faraday Soc.* 54, 1069–1073.

DARKEN, L. S., AND R. W. GURRY (1945) The system iron-oxygen I. The wüstite field and related equilibria. *J. Amer. Chem. Soc.* 67, 1398–1412.

RAO, C. N. R. (1961) Kinetics and thermodynamics of the crystal structure transformation of spectroscopically pure anatase to rutile. *Can. J. Chem.* 39, 498–500.

SHANNON, R. D. (1964) Kinetics and mechanism of the anatase-rutile transformation. *AEC Rep. No.* **UCRL**-11001, 97 pp. (*Chem. Abstr.* 63, 2468b).

———, AND J. A. PASK (1964) Topotaxy in the anatase-rutile transformation. *Amer. Mineral.* 49, 1707–1717.

———, AND ——— (1965) Kinetics of the anatase-rutile transformation. *J. Amer. Ceram. Soc.* 48, 391–398.

SPURR, R. A., AND H. MYERS (1957) Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer. *Anal. Chem.* 29, 760–762.