

Hydrogen Reaction Mechanisms on TiO₂

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A kinetic study of the ortho-para hydrogen conversion and the hydrogen-deuterium equilibration reaction was made on the anatase form of TiO₂, over the temperature range 93° to 773°K. The products of the conversion reaction were analyzed by microthermal conductivity and those of the equilibration reaction by mass spectrometry. Three distinct temperature regions of activity were found and the results are discussed in terms of a low-temperature physical mechanism, a high-temperature chemical mechanism, and the nature of the surface sites on TiO₂.

INTRODUCTION

The comparison of the kinetics of the hydrogen-deuterium exchange reaction and the para-ortho hydrogen conversion reaction provide a useful basis for the study of solid surfaces. The H₂-D₂ exchange takes place via a chemical mechanism, involving the formation of a bond between an adsorbed species and the surface. Depending upon the temperature, the parahydrogen conversion may take place via a chemical mechanism or a physical one, in which paramagnetic surface sites can cause a change in the nuclear spin of the hydrogen molecule.

In the present work these two reactions, H₂-D₂ exchange and parahydrogen conversion, have been used to study the nature of the surface of the anatase form of TiO₂.

A review of the kinetics of these reactions, pressure dependencies, and the effect of the difference in zero-point energies of the H₂ and D₂ molecules has been given previously (1). Considerations of the relation between the activity of a porous catalyst and grain size have been discussed by Thiele (2) and Wheeler (3).

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Two possible chemical mechanisms must be considered. These are conventionally referred to as the Bonhoeffer-Farkas mechanism (4), involving reaction between two adjacent chemisorbed species, and the Eley-Rideal mechanism (5), involving reaction between a chemisorbed species and a physically adsorbed species held in a van der Waals layer above the chemisorbed film.

The physical conversion of parahydrogen to orthohydrogen may proceed by three possible mechanisms: collisional, vibrational, or translational. The collision treatment was proposed by Wigner (7). Ashmead, Eley, and Rudham (6) have interpreted the vibrational mechanism according to the original work of Sandler (8). In this mechanism the variation in transition probability when an adsorbed hydrogen molecule vibrates perpendicular to the surface is considered. Each vibration is equivalent to a collision and the transition probability is increased. The translational mechanism due to Harrison and McDowell (9) assumes that the surface contains a number of paramagnetic centers separated by inactive areas. The adsorbed layer is regarded as a two-dimensional gas so that the adsorbed molecule may move freely on the surface.

The temperature dependence of the absolute rate of physical conversion, k_m , will be governed by the Arrhenius equation.

Using this equation Eley (10) has discussed the relationship between the apparent activation energy, E_a , and the heat of adsorption for cases where the Langmuir or the Freundlich isotherms are obeyed.

EXPERIMENTAL

The equilibration and conversion reactions were carried out in a conventional vacuum system capable of achieving a vacuum of 10^{-7} torr. The apparatus and method of parahydrogen preparation and analysis have been described previously (1).

The products of the H₂-D₂ equilibration were analyzed in a Consolidated Electro-dynamics Company model 21-62A mass spectrometer.

Gould *et al.* (11) have stated that there are nine possible types of positive ions which may be formed from hydrogen-deuterium mixtures in the mass spectrometer, and Bleakney (12) has discussed the probabilities of ionization of the hydrogen molecule and reports that the velocity of the impinging electrons may be adjusted so that monatomic ions are not produced. Analysis of pure hydrogen, deuterium, and hydrogen-deuterium mixtures over a wide range of inlet pressures resulted in spectra which showed no contribution from monatomic or triatomic species. Therefore, it was concluded that the intensities observed at mass-to-charge ratios of 2, 3, and 4 were due solely to (HH)⁺, (HD)⁺, and (DD)⁺, respectively. The composition of mixtures containing these three species was determined directly from the measured intensities after correction for instrument background.

The equilibrium concentration of hydrogen deuteride depends on the initial composition of the reactants and the temperature of the reaction. It was calculated from the equilibrium constant, K , for the equilibrium reaction which may be written as follows:

$$K = \frac{[\text{HD}]_{\infty}^2}{[\text{H}_2]_{\infty}[\text{D}_2]_{\infty}}$$

The reproducibility of the mass spectrometer was checked by repeated analysis of a mixture of H₂, HD, and D₂. The

average percent deviation between the intensities at mass-to-charge ratios of 2, 3, and 4 was 0.76%, 0.22%, and 0.78%, respectively. These deviations are caused by errors in reading the spectrum and by changes in the sensitivity of the instrument as the inlet pressure changes. A cryostat was used to obtain reaction temperatures below room temperature, and could be controlled to $\pm 0.1^\circ\text{C}$. For reactions above room temperature the lower half of the cryostat was removed and the reaction vessel placed in a small electric furnace.

A theoretical value for the equilibrium constant, K , was obtained from the formula of Urey and Rittenberg (13). The experimental rate constants measured at temperatures above 300°C were corrected for the reaction taking place due to catalysis by the reaction vessel (14, 15).

CHARACTERIZATION OF MATERIALS

Spectrochemical analysis showed the TiO₂ to be at least 99.5% pure, with the principal impurity being aluminum, which will reduce the free electron component of anatase. No paramagnetic impurities in excess of 0.001% were observed. X-Ray diffraction showed at least 95% of the anatase form of TiO₂ was present. The surface area, as determined by the usual BET low-temperature nitrogen adsorption, was 8.58 m²/g.

The presence of surface hydroxyl groups has been shown to be of importance in effecting the equilibration reaction (16). In an attempt to determine qualitatively the effect of the bake-out procedure on surface hydroxyl groups transmission infrared analysis was carried out. Discs approximately 75 μ thick were formed from the TiO₂ powder by pressing in a steel die.

The pressed discs of anatase were supported in a quartz tube, which was then evacuated and baked out at 500°C for 12 hr, sealed off, and removed from the vacuum system for analysis. The results are shown in Fig. 1, together with those of similar work of Yates (16). The spectrum before bakeout, curve 1, had a shoulder at 3720 cm^{-1} due to the vibration of isolated hydroxyl groups on the surface, and a broad band centered at 3400 cm^{-1} due to

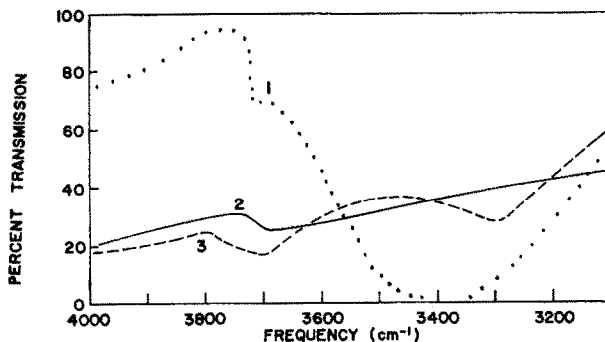


Fig. 1. Infrared spectra for anatase: 1, as received. 2, after bakeout at 500°C for 12 hr *in vacuo*; 3, after bakeout at 350°C *in vacuo* (ref. 16).

hydrogen bonding between hydroxyl groups and physically adsorbed water. After bake-out, curve 2, the broad band at 3400 cm^{-1} disappeared leaving a small band at 3720 cm^{-1} . Yates' results (16), curve 3, are for anatase baked out at 350°C.

The upper limit stability of the anatase form is 915°C, where it transforms to rutile (17). However, different methods of preparation of the anatase form and impurity concentrations have been found to give much lower transformation temperatures (18). In the present work, the samples were found to have retained the anatase form after the completion of the experimental runs.

RESULTS

The parahydrogen conversion and $\text{H}_2\text{-D}_2$ equilibration reactions were found to obey first order kinetics at all temperatures, studied. A typical plot is shown in Fig. 2, where Ω_0 and Ω_t are the micro-Pirani thermal conductivity gauge resistance values for the reaction mixture initially and after time t . These values are directly proportional to the parahydrogen content of the mixture (4). Samples of the order of 5 g of catalyst were used with reaction vessel volumes of the order of 150 cc.

Hydrogen-Deuterium Equilibration

The temperature dependence of the absolute rate constant for equilibration on anatase at a constant pressure of 10 torr, from 93° to 773°K, is shown in Fig. 3. The curve obtained with increasing temperature

shows several prominent features. A low activity for equilibration was found at 93°K. This activity increased to a maximum at 123°K. A second maximum occurred near 173°K with a subsequent rapid decrease of activity as temperature was increased to 298°K. The exact position of this minimum of activity was difficult to determine because of the small amount of product resulting from the reaction.

The activities obtained with decreasing temperature agreed with those obtained with increasing temperature down to 473°K. Further temperature decreases through the region of minimum activity resulted in increased rates of reaction. The activity

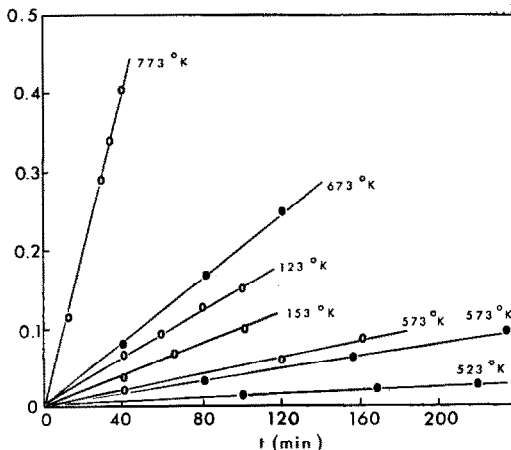


Fig. 2. Equilibration and conversion reactions, showing first order nature: O, conversion reaction, ordinate $2.303 \log(\Omega_0/\Omega_t)$; ●, equilibration reaction, ordinate $2.303 \log[(\text{HD}_a - \text{HD}_0)/(\text{HD}_a - \text{HD}_t)]$.

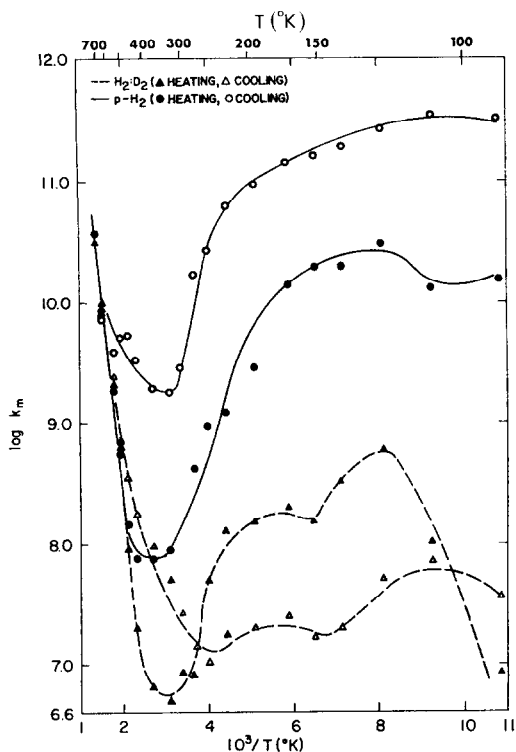


Fig. 3. Temperature dependence of equilibration and conversion reactions ($p = 10$ torr).

then rose slowly through the low-temperature region but was a factor of 5 less than that obtained with increasing temperature.

It was thought that the high-temperature reaction might have reduced the low-temperature activity of anatase for the equilibration reaction. Therefore, the sample was again baked out and cooled to 93°K. A second series of measurements covering the 93–273°K region were made, and although the low-temperature activity increased it did not reach the level previously obtained. The two definite maxima of activity were again observed and this activity did not decrease on cooling from 273°K.

Apparent activation energies, E_a , may be obtained from the slopes of the Arrhenius plots. The values of E_a in the region of falling activity between 173° and 298°K were less than 1 kcal/mole and negative. Above room temperature the values were positive and from 1 to 7 kcal/mole below 423°K and in the range of 10–20 kcal/mole above this temperature.

Assuming that a Freundlich isotherm was valid for the adsorptive processes involved here, the kinetic order of the reaction, n , was determined from a plot of $\log k_m$ versus $\log P$ at constant temperature (1).

The pressure dependency of the equilibration reaction was measured over a range of 2–25 torr and a typical plot is shown in Fig. 4 for the high-temperature region. At high temperatures the reaction was first order at all temperatures. The low-temperature data indicated that the reaction order was changing from first order at pressures less than 10 torr to zero order at pressures greater than 10 torr. The surface was becoming more saturated with hydrogen as the pressure was increased.

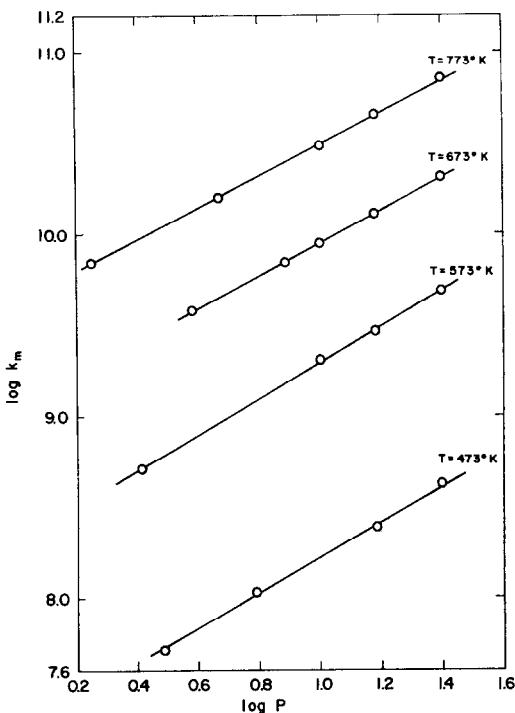


Fig. 4. Pressure dependence of equilibration reaction at high temperatures.

Parahydrogen Conversion

Experiments similar to those performed using the equilibration reaction were made on anatase using parahydrogen. The temperature dependence of the rate constant is compared graphically with the results ob-

tained for the equilibration reaction in Fig. 3.

The activity of anatase for the parahydrogen conversion at low temperatures was one to two orders of magnitude greater than that found for the equilibration reaction. There was a trend towards decreasing activity from 93° to 373°K. This activity did rise sharply between 108° and 123°K. Between 473° and 773°K results similar to those obtained for the equilibration reaction were obtained. Data taken with decreasing temperature again showed a rise in activity in the 523–323°K region. Further decreases in temperature resulted in a continuous increase in activity which was greater than that obtained with increasing temperature.

Apparent activation energies for the conversion reaction on anatase were, in general, negative and increasing in magnitude through the temperature range 93° to 373°K. At high temperatures the apparent activation energies were similar to those found for the equilibration reaction. The pressure dependencies of the absolute rate constant for conversion showed a linear form similar to Fig. 4. In the high-temperature region (523–773°K) the reaction order was close to unity, while in the low-temperature region (93–198°K) the reaction order was fractional and close to 0.7.

DISCUSSION

The temperature dependence of the absolute rate constants for parahydrogen conversion and hydrogen–deuterium equilibration on anatase can be separated into three regions: (1) a low-temperature region, $T < 200^\circ\text{K}$, where the rate of conversion is considerably greater than the rate of equilibration; (2) an intermediate region, $200^\circ\text{K} \leq T \leq 473^\circ\text{K}$, where the rates of both reactions decrease to a minimum; (3) a high-temperature region, $T > 473^\circ\text{K}$, where the rates of conversion and equilibration are approximately the same. In all cases considered, the calculation of a diffusion-controlled rate constant showed that the experimental rate constants could be attributed to reaction on the surface only and not in pores.

Low-Temperature Region

At low temperatures the rate of parahydrogen conversion would be expected to be greater than the rate of hydrogen–deuterium equilibration even in the case where both reactions were proceeding by the same mechanism, i.e., a chemical mechanism. This is due to the difference in zero point energies of hydrogen and deuterium, which is 1789 cal. If this entire energy is effective in the reaction, then the maximum amount of separation in the rates of conversion and equilibration will be given by $\exp(1789/RT)$ (1).

The parahydrogen conversion at low temperatures shows the general decrease in rate of reaction with increasing temperature which is characteristic of a physical mechanism. Sandler (19) has obtained similar results for rutile in the range 90–195°K.

According to Sandler, the paramagnetic sites responsible for the physical conversion are due to oxygen deficiencies and extra electrons left on the surface. These sites may also be considered to be Ti^{3+} ions and are created during the thermal activation of the rutile or anatase. The loss of oxygen is accompanied by a change in the color of the oxide from white to blue. Paramagnetic sites created in this manner would also account for the increased rate of conversion at low temperatures found on cooling from high temperatures. The exposure of anatase to parahydrogen at high temperature served to further reduce the surface, creating an additional number of paramagnetic sites.

The rise in the rate of conversion obtained on heating between 108° and 123°K may be due to an energy of activation required for migration of the hydrogen on the surface to a paramagnetic site of more difficult accessibility. It may also have been caused by a small contribution due to a chemical mechanism. A low-temperature maximum in the equilibration reaction occurs in this same region of temperature.

Of the three mechanisms which have been proposed for the physical conversion of parahydrogen, the vibrational mechanism seems to agree best with the experimental

results found for anatase. The translational mechanism predicts a positive activation energy for the reaction, while negative energies have been observed at these temperatures. The collision mechanism predicts negative activation energies of the order of 100 cal/mole or less, and a direct dependence of the rate of conversion on pressure.

The theoretical rate expression for the vibrational mechanism may be calculated from the work of Ashmead, Eley, and Rudham (6), as

$$k_m = 1.129 \times 10^{-9} [\mu_a^2 n_s \theta \nu G(T) / r_s^6 T] \quad (1)$$

The factor of 1.129×10^{-9} accounts for the constant terms in the overall efficiency and allows the substitution of μ_a in Bohr magnetons and r_s in angstroms. The amount of molecular hydrogen adsorbed, $n_s \theta$, is taken as 10^{12} molecules/cm² and the distance of closest approach, r_s , as 2 Å. $G(T)$ at 93°K was calculated to be 0.2770 and, μ_a , the magnetic moment of one unpaired electron is 1.73 Bohr magnetons. Dewing and Robertson's (20) value of 4.5×10^{11} sec⁻¹ is taken for ν . The value of k_m at 93°K calculated on this basis is 7.1×10^{10} molecules/cm² sec, which is in good agreement with the experimental value of 1.5×10^{10} molecules/cm² sec.

If the collision mechanism is, in fact, valid, then a theoretical value for the absolute rate of conversion may be calculated (6). At 93°K this value is 4.9×10^9 molecules/cm² sec, assuming that all of the surface is active. It is usually found that only a small fraction, of the order of 0.001, of the surface of oxides is catalytically active (21). This would reduce the rate for the collision mechanism to values which would be masked by any adsorptive process.

The low-temperature equilibration reaction on anatase must take place by a chemical mechanism. The kinetic order of the reaction changed from a first order reaction below 10 torr to a zero order reaction at pressures greater than 10 torr. The temperature dependence of the reaction was measured at 10 torr and the reaction can be considered to be first order. First order kinetics and the small positive activation

energies, 2–4 kcal/mole, favor an Eley-Rideal type mechanism. A Bonhoeffer-Farkas mechanism or the direct interchange of gas molecules with adsorbed atoms on the surface according to the original Rideal mechanism would not be expected at these low temperatures. The Eley-Rideal mechanism in which the activated complex is formed from chemisorbed atoms on the surface and molecules held in a van der Waals layer is more probable at low temperatures.

The two temperatures at which maximum values for the rate constant were observed, 123° and 173°K, may indicate the presence of different types of sites on which the reaction occurs. Kinetic measurements do not give an insight into the exact nature of these sites. However, they may be Ti³⁺ ions located in lattice positions requiring different energies of accessibility. Above room temperature the hydrogen is more strongly adsorbed than at low temperatures. The bonding is probably of a covalent nature with the *d* electron of Ti³⁺. This stronger bonding above room temperature reduced the low-temperature activity of the sample which had been exposed to hydrogen above room temperature and then cooled to low temperature. The sample which was only exposed to hydrogen at low temperatures retained most of its activity on cooling.

Intermediate Temperature Region

The rapid decrease in activity for both the equilibration reaction and the conversion reaction at temperatures above 200°K is due to the desorption of hydrogen from the surface. The higher activities observed with decreasing temperature in this region for both reactions arises from the presence of chemisorbed hydrogen atoms which are absent at increasing temperatures and are taken up by the surface during the cooling process. Similar results have been observed on rare earth oxides for the parahydrogen conversion in this temperature region (22).

Adsorbed hydrogen taken up on cooling from high temperatures reduces the activity of anatase for the equilibration reaction at low temperatures. This is shown by the fact that the anatase which was heated only to

273°K retained its original activity with decreasing temperature.

High-Temperature Region

At temperatures above 473°K the rates of equilibration and conversion on anatase are similar, indicating that a chemical mechanism is involved in both reactions. The mechanism is probably of the Bonhoeffer-Farkas type involving dissociation of molecules on the surface and their subsequent recombination. The kinetic order for reactions taking place by this mechanism should vary from first order at low surface coverage to zero order at high coverage. First order kinetics were observed for the equilibration reaction and fractional orders near to one for the conversion reaction. Alternatively, a mechanism of the original Rideal type would give first order kinetics on a saturated surface. Laidler (23) has shown that this mechanism is only valid for free radical recombination reactions and favors the Bonhoeffer-Farkas mechanism for exchange reactions of the type investigated in this work.

At high temperature the rate of equilibration on anatase may be represented by the equation

$$k_m = 2.5 \times 10^{11} \exp(-13\,300/RT) \quad (2)$$

where 13 300 is the apparent activation energy in cal/mole and 2.5×10^{11} is the frequency factor in units of molecules/cm² sec. If the dissociative adsorption of hydrogen is rate-controlling, then according to Ashmead *et al.* (6) the expression for the absolute rate is given by

$$k_m = ZaF_a(1 - \theta_H)^2 \exp(-E_a/RT) \quad (3)$$

where $(1 - \theta_H)^2$ is the fraction of dual sites available on the surface, F_a is the fraction of these sites which are active, a is the sticking coefficient, and Z , the collision number. The value of $(1 - \theta_H)$ is given by the reaction order, n . A collision number of 3.64×10^{22} molecules/cm² sec was calculated. The sticking coefficient was taken as 0.1 and value of 0.001 was assumed for F_a . The calculated value of k_m was 1.65×10^{14} mole-

cules/cm² sec, which is considerably higher than the experimental value of 8.2×10^9 molecules/cm² sec. Lower values of the active fraction of the surface are not very probable, and it must be concluded that the rate of dissociative adsorption of hydrogen is not rate-controlling. It has been suggested that the adsorption of hydrogen or deuterium on isolated double sites would cause the observed rates to be lowered (21).

REFERENCES

- HARRIS, J. R., AND ROSSINGTON, D. R., *J. Am. Ceram. Soc.* **51**, 511 (1968).
- THIELE, E. W., *Ind. Eng. Chem.* **31**, 916 (1939).
- WHEELER, A., "Catalysis" (P. H. Emmett, ed.), Vol. 2, p. 105. Reinhold, New York, 1955.
- FARKAS, A., "Orthohydrogen, Parahydrogen and Heavy Hydrogen." Cambridge Univ. Press, Cambridge, England, 1935.
- ELEY, D. D., AND RIDEAL, E. K., *Proc. Roy. Soc. (London)* **A178**, 429 (1941).
- ASHMEAD, D. R., ELEY, D. D., AND RUDHAM, R., *Trans. Faraday Soc.* **59**, 207 (1963).
- WIGNER, E., *Z Physik. Chem. (Leipzig.)* **B23**, 28 (1933).
- SANDLER, L., *Can. J. Chem.* **32**, 249 (1954).
- HARRISON, L. G., AND MCDOWELL, C. A., *Proc. Roy. Soc. (London)* **A220**, 77 (1953).
- ELEY, D. D., *Nature* **194**, 1076 (1962).
- GOULD, A. J., BLEAKNEY, W., AND TAYLOR, H. S., *J. Chem. Phys.* **2**, 362 (1934).
- BLEAKNEY, W., *Phys. Rev.* **35**, 1180 (1930).
- UREY, H. C., AND RITTENBERG, D., *J. Chem. Phys.* **2**, 48 (1934).
- ANNIS, G. S., CLOUGH, H., AND ELEY, D. D., *Trans. Faraday Soc.* **54**, 394 (1958).
- MIYAHARA, K., AND TSUMURA, A., *J. Res. Inst. Catalysis, Hokkaido Univ.* **9**, 42 (1961).
- YATES, D. J. C., *J. Phys. Chem.* **65**, 746 (1961).
- KIRK, R. E., AND OTHMER, D. F., "Encyclopedia of Chemical Technology," Vol. 12, p. 268. Interscience, New York, 1954.
- PAMFILOV, A. V., MUSHII, R. YA, AND MAZURKEVICH, YA, S., *Ukr. Khim. Zh.* **28**, 58 (1962).
- SANDLER, Y. L., *J. Phys. Chem.* **58**, 54 (1954).
- DEWING, J., AND ROBERTSON, A. J. B., *Proc. Roy. Soc. (London)* **A240**, 423 (1957).
- ACRES, G. J. K., ELEY, D. D., AND, TRILLO, J. M., *J. Catalysis* **4**, (1965).
- ASHMEAD, D. R., ELEY, D. D., AND RUDHAM, R., *J. Catalysis* **3**, 230 (1964).
- LAIDLER, K. J., *J. Phys. Chem.* **55**, 1067 (1951).