

the pipet. Since the pipet was suspended by means of nylon strings, it was possible to shake the liquid. In fact, a few times it was observed that the meniscus splattered on shaking, however, no visible opalescence occurred. The only conditions under which one could obtain momentary opalescence was by cooling the system rapidly. The opalescence persisted for only a few seconds after cooling was stopped.

From Mayer's¹² and Rice's¹³ theories of liquids in the critical region, one would expect opalescence to occur due to differences in density at the critical point. Failure to observe opalescence, therefore, indicates either that the theories are incorrect or that the density differences are particularly small for hydrogen.

It is interesting to note that our own direct measurements of critical pressure and of critical temperature are in close agreement with those computed at Leiden,⁸ from data of state. Values of critical temperature differ by only 0.07°. Since the Leiden data were obtained from the P - V isotherm for which a flat portion occurs (as well as from the vapor pressure data), it appears that, in the case of hydrogen, no flat portions exist above

the critical or that the temperature range over which they do exist is extremely small. The former description would contradict the Mayer theory, but is consistent with the Rice theory which does not postulate isotherms with flat portions above the observed critical temperature and pressure. This subject will be further investigated in connection with the high pressure P - V - T program now under way in this Laboratory for a number of gases and liquids.

Acknowledgment.—We wish to acknowledge the helpful suggestions of Mr. L. E. Cox, Shop Foreman of the Cryogenic Laboratory, in the design and construction of the apparatus.

Summary

A new apparatus has been constructed to measure accurately and directly critical constants of condensed gases. The critical constants of normal hydrogen have been determined and found to be 33.244°K. and 12.797 atmospheres. The vapor pressure of normal hydrogen in the immediate vicinity of the critical temperature has also been measured.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ILLINOIS INSTITUTE OF TECHNOLOGY]

The Kinetics of the Zirconium-Nitrogen Reaction at High Temperatures

BY ANDREW DRAVNIKS¹

Introduction

Zirconium is known to react with most gases.²⁻⁵ Nitrogen is taken up in a solid solution with only slight expansion of the zirconium lattice. Under suitable conditions a thin nitride film is also formed on the surface of the metal phase.⁶ Hayes and Roberson⁶ measured the hardening of the metal caused by nitrogen in solid solution. Recently Gulbransen and Andrew⁷ investigated the

kinetics of the nitrogen uptake by zirconium at temperatures up to 850°, and observed no film formation under conditions employed.

In the present work a kinetic study has been made of the zirconium-nitrogen reaction at higher temperatures where a well-defined zirconium nitride phase is formed in addition to a solution of nitrogen in zirconium metal.

Experimental

The rate of the nitrogen-zirconium reaction was measured by observing the pressure decrease in the apparatus shown schematically in Fig. 1. A silica glass tube A, containing the specimen, was connected by a graded seal to a Pyrex ground joint B and inserted into a continuously evacuated silica glass jacket C. The vacuum jacket prevented the passage of air through the silica and, hence, kept the nitrogen atmosphere in the inner tube free of oxygen at temperatures up to 1050°. The specimen D was hooked on the end of a silica glass rod supplied with a sealed-in iron rod E. The rod and specimen were introduced through the end of the glass tube F which was then sealed. With the specimen in the cold part of tube A, the system was evacuated to 10⁻⁶ mm., then nitrogen was introduced by immersing a capillary, through which the gas was flowing, so as to touch the porous glass plate under the mercury seal G. The pressure in the system was read on mercury manometer H to ±0.05 mm. with a cathetometer.

A strong current of air was blown by an electric fan on the parts of apparatus outside the furnace; temperature readings of the air were taken in order to correct for the small changes in room temperature. To start a run, a specimen was pushed by means of a magnet into the hot zone and pressure measurements begun.

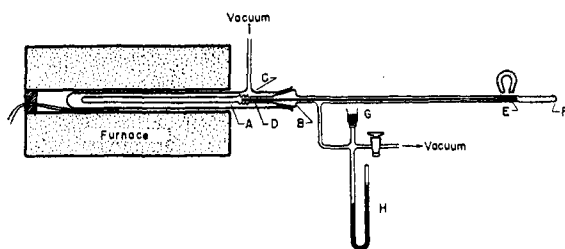


Fig. 1.—Apparatus for measuring gas-metal reaction rates.

- (1) Standard Oil Company (Ind.), Chicago, Illinois.
- (2) J. H. DeBoer and J. D. Fast, *Rec. trav. chim.*, **55**, 459 (1936).
- (3) J. D. Fast, *Metallwirtschaft*, **17**, 641 (1938).
- (4) J. H. DeBoer and J. D. Fast, *Rec. trav. chim.*, **59**, 161 (1940).
- (5) W. G. Guldner and L. A. Wooten, *J. Electrochem. Soc.*, **93**, 223 (1948).
- (6) E. T. Hayes and A. H. Roberson, *J. Electrochem. Soc.*, **96**, 142 (1949).
- (7) E. A. Gulbransen and K. F. Andrew, *AIME, J. of Metals*, **165**, 515 (1949).

Furnace temperatures were maintained within $\pm 3^\circ$ during a run by means of a Wheelco Capacitrol. From a calibration of the apparatus, a 1-mm. pressure change corresponded to approximately 0.1 mg. nitrogen uptake, and the estimated accuracy for each measurement was ± 0.01 mg. of nitrogen per specimen. Specimens with areas of 3–5 sq. cm. were used.

Nitrogen of pre-purified quality (Matheson Co., Inc.) was used; according to the specification, impurities of oxygen and hydrogen were less than 0.001%. Zirconium sheet of 0.05 mm. (2 mil) thickness—in a few cases 0.125 mm. (5 mil)—was used. The metal was obtained from the Foote Mineral Company. A typical analysis of the zirconium was:

Hf	2.5–3.0%	O ₂	0.03%
Fe	0.04%	N ₂	0.01%

Results

The reaction between zirconium and nitrogen was investigated from 362 to 1043° and from 10 to 300 mm. nitrogen pressure. In most cases the square of the nitrogen uptake per cm.² of surface, plotted *versus* time gave a straight line indicating that the parabolic law^{8–13} $m^2 = kt$ was obeyed. Here m is nitrogen uptake in g. per sq. cm. of surface and t the time in seconds.

Table I shows the parabolic rate constants k for several temperatures and pressures. Figure 2 illustrates the rate law for some of the experiments. Figure 3 shows the reaction curves for experiments of long duration at 897° and several

TABLE I
PARABOLIC RATE CONSTANTS FOR THE NITROGEN-ZIRCONIUM REACTION

Temp., C.	Nitrogen pressure, mm. ^a	Parabolic rate constant g. ² cm. ⁻⁴ sec. ⁻¹ $\times 10^{12}$
862	20–10	0.20
862	80–70	0.22
890	80–65	0.51
920	70–50	1.1
928	70–50	1.1
968	50–30	2.0
989	50–30	2.7
998	50–30	4.0
998	50–30	3.1
1007	50–30	4.6
1007	50–30	4.0
1043	80–60	6.8
1043	20–10	6.9
999	70–50	13 ^b
928	70–50	1.9 ^c
896	70–50	1.6 ^d

^a Limits indicate pressure at start and end of experiment.

^b Different sample of zirconium, of 0.125 mm. thickness.

^c After an initial oxidation of 0.040 mg. oxygen per cm.² surface.

^d In a single-walled silica glass tube; the color of the nitride layer was grayish-yellow, indicating a leak of oxygen through the walls from outside.

(8) G. Tammann, *Z. anorg. allgem. Chem.*, **111**, 78 (1920).

(9) K. Fischbeck, L. Neundenbel and F. Salzer, *Z. Elektrochem.*, **40**, 517 (1934).

(10) H. A. Miley, *Trans. Electrochem. Soc.*, **81**, 391 (1942).

(11) U. R. Evans, *ibid.*, **83**, 335 (1943).

(12) C. Wagner, *Z. physik. Chem.*, **B21**, 25 (1933).

(13) C. Wagner and K. Grunewald, *ibid.*, **B40**, 455 (1938).

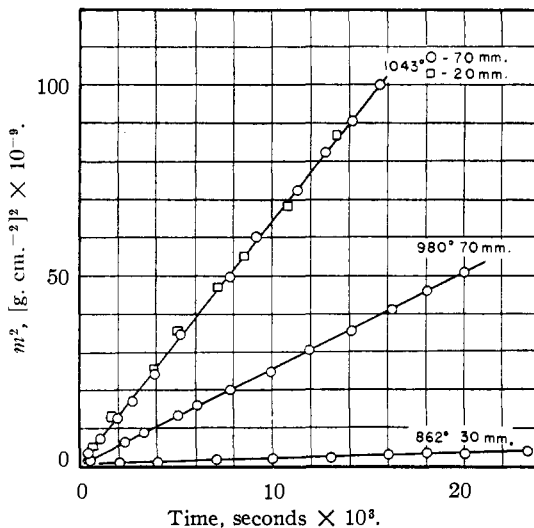


Fig. 2.—Rates of zirconium-nitrogen reaction.

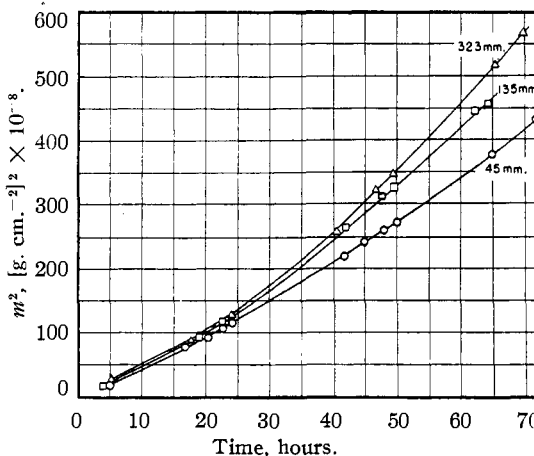


Fig. 3.—Reaction of nitrogen with zirconium at 896°, long exposures; figures indicate nitrogen pressure.

pressures; since the samples for this set of experiments were cut from different zirconium sheet, the rate constants from Fig. 3 cannot be compared directly with those in Table I.

Discussion

Gulbransen and Andrew⁷ have reported that at temperatures up to 800° and reaction times up to 150 minutes, the zirconium-nitrogen reaction obeyed the parabolic law; however, no detectable film of nitride formed on the surface, as opposed to the oxidation reaction of zirconium where an oxide scale developed. In the present study of zirconium-nitrogen reaction at temperatures of 862 to 1043°, golden-yellow and tenaciously adherent nitride films were observed. These films showed a weak zirconium nitride X-ray pattern.

According to Gulbransen, for the zirconium-oxygen reaction the over-all rate of oxygen absorption still remains parabolic if the rates of both the penetration of gas into metal and the growth of

oxide layer are diffusion-controlled and the diffusion constants remain constant. This seems to be the case also in the zirconium-nitrogen reaction during the initial period of reaction, as shown by the curves in Fig. 2. Although nitrogen diffuses into the metal and also precipitates as a nitride film, the rate is parabolic. Film thicknesses were determined by a microscopic investigation of the specimens. The nitride films formed were very thin, the thickness being well below one micron even in cases of nitrogen uptake up to 0.5 mg. per sq. cm. of surface, indicating that the major part of the nitrogen was used in the formation of the solid solution of nitrogen in zirconium.

To obtain an idea of the continuity of the nitride film, small specimens kept at temperatures between 900 to 1000° were covered with a nitride film and exposed to small amounts of oxygen. The adsorption of oxygen started without any apparent induction period; hence, the nitride film was either porous or so thin that the penetration by oxygen was too fast for observation.

In the first case, the parabolic law would be conditioned by diffusion of nitrogen in zirconium, the film pore resistance adding only a small term to the over-all rate expression. However, as pointed out by Gulbransen^{7,8} under pure no-film conditions one would expect a square root dependence of the diffusion rate on the pressure of gas. In the present study, as shown by the data in Table I and the initial parts of the curves in Fig. 3, the rate of nitrogen uptake does not depend markedly on nitrogen pressure, in agreement with Gulbransen's results at lower temperatures.

The following two explanations remain open to relate the results of kinetic study: (1) the nitride film is essentially porous but there is a continuous extremely thin protective film on the bottom of the pores; this film provides for the

pressure independency but contributes a relatively unimportant term to the over-all rate, which is then controlled by diffusion of nitrogen in zirconium metal; (2) the nitride film is essentially continuous throughout its thickness and the over-all rate is determined by both diffusion in metal and film, both processes having comparable importance.

When the zirconium-nitrogen reaction was continued long enough, some pressure dependence appeared, as illustrated by Fig. 3. The rate law was no longer parabolic but deviated toward the linear. An examination of the specimens showed that profound structural changes occurred at about the same time that the deviations in the curves became prominent. The specimens after prolonged exposure were very brittle, warped, and showed measurable changes in dimension. Pin hole X-ray diffraction patterns indicated that the metal grains had grown, the lattice constants had changed, and the grains appeared strained. Under a microscope the surface of the specimen seemed to have an island structure of nitride film, suggesting that cracks had formed and healed. Changes of this character were not detected on specimens subjected to reaction for shorter lengths of time—*i.e.*, while the reaction was still parabolic.

Thus the deviations from the initially parabolic rates observed in the long runs were probably due to swelling of the zirconium metal. A volume increase is caused by nitrogen when the latter approaches saturation in the metal,²⁻⁴ in turn causing cracking of the hard nitride film so that its protective action is less efficient.

From Fig. 4 one sees that on a $\log k$ versus reciprocal temperature graph the comparable parabolic rate constants lie on an approximately straight line, whose slope indicates an activation energy of 52 kcal. per mole. Below 900° the points deviate toward higher values of activation energy, indicating a possible change in the reaction mechanism. The change may be associated with the $\alpha \rightarrow \beta$ transition of zirconium metal at 865°¹⁴; this transition point spreads out to a transition region in the vicinity of 900° if nitrogen or other gases are dissolved in zirconium.²

The presence of oxygen either introduced into the specimen prior to reaction or leaking in during the reaction tended to increase the rate of nitrogen uptake.

Acknowledgment.—The research work reported in this paper was done under contract with U. S. Navy Office of Naval Research.

Summary

The kinetics of the zirconium-nitrogen reaction were studied between 862 to 1043°. The initial rate obeys the parabolic law with an activation energy of 52 kcal. and is independent of pressure.

(14) J. H. Boer, P. Clausing and J. D. Fast, *Rec. trav. chim.*, **55**, 450 (1936).

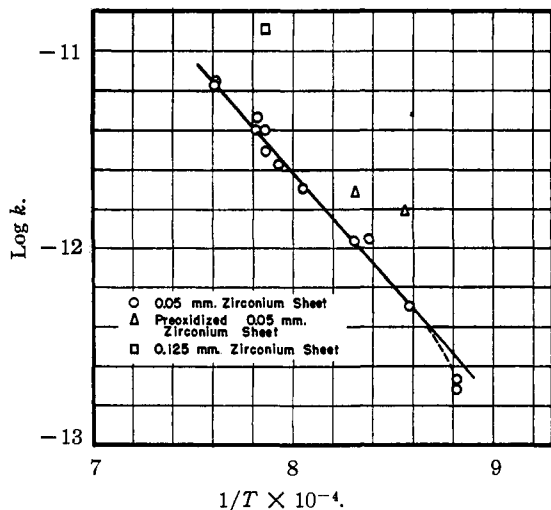


Fig. 4.—Variation of rate constant with temperature for zirconium-nitrogen reaction.

For reactions of long duration the rate increased compared to the initial parabolic rate, this change was probably due to volume changes of the metal

phase. The rate constants are sensitive to the origin of zirconium samples.

CHICAGO, ILLINOIS

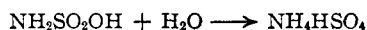
RECEIVED FEBRUARY 8, 1950

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

The Kinetics of Hydrolysis of the Sulfamate Ion

BY SAMUEL H. MARON AND ALAN R. BERENS

Sulfamic acid in aqueous solution and at elevated temperatures hydrolyzes according to the scheme¹



The extents of hydrolysis of the acid in fairly concentrated solutions were measured by Cupery² and by Oberhauser and Urbina,³ but these men made no attempt to analyze the kinetics of the reaction.

Neutral or alkaline aqueous solutions of salts of this acid are stable even when boiled. However, on acidifying such solutions hydrolysis is again observed. It would appear, therefore, that the presence of hydrogen ions is necessary for hydrolysis of the sulfamate ion. The purpose of the present study was to investigate this effect of hydrogen ions on the rate of hydrolysis, and to elucidate the kinetics of the reaction.

Experimental

The rate of hydrolysis was followed by periodic removal of samples of reaction mixtures and analyzing them for sulfamate content. The analytical procedure employed was titration with standard sodium nitrite according to the procedure of Bowler and Arnold,⁴ using starch iodide solution as an external indicator.

Materials.—The sulfamic acid and ammonium sulfamate used were the "Pure, Standardized" products of the Lamotte Chemical Co. After drying for twenty-four hours under vacuum at 40°, the sulfamic acid was found to be 100.0% pure by titration with standard sodium hydroxide.

The standard 0.05 molar solutions of sodium nitrite were made slightly alkaline with sodium hydroxide to prevent loss of nitrous acid. Nitrite solutions so prepared were stable for several months. They were standardized against a potassium permanganate solution according to the procedure given by Kolthoff and Sandell.⁵

The starch iodide solution used as indicator was prepared as follows. Five grams of starch and 20 g. of zinc chloride were dissolved slowly in 100 ml. of water. After the mixture was boiled for two hours, 2 g. of potassium iodide was added, the solution filtered through sintered glass, and then diluted to one liter. The resulting indicator solution was of such sensitivity that 0.02 ml. of 0.05 molar sodium nitrite solution in 100 ml. of dilute sulfuric acid was sufficient to give a distinct blue coloration in a spot-test. The indicator blank correction was therefore negligible.

(1) E. Divers and T. Haga, *J. Chem. Soc.*, **69**, 1634 (1896).

(2) M. E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

(3) Oberhauser and Urbina, *Anales facultad filisof. y educacion. Univ. Chile, seccion quim.*, **3**, 119 (1948).

(4) W. W. Bowler and E. A. Arnold, *Anal. Chem.*, **19**, 336 (1947).

(5) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 574.

Apparatus.—The thermostat was an oil-bath controlled by a sensitive mercury thermoregulator to within $\pm 0.05^\circ$ in the range 80–100°. Reaction vessels were rubber-stoppered 500 and 1000 ml. erlenmeyer flasks. All volumetric apparatus was calibrated at each temperature employed.

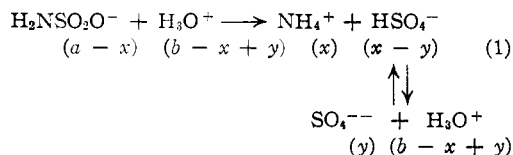
Procedure.—To prepare reaction mixtures, weighed amounts of sulfamic acid, or sulfamic acid and ammonium sulfamate, were dissolved in distilled water or hydrochloric acid solutions preheated to the desired temperature in the thermostat. The reaction mixture was immediately stirred and the first sample pipetted out. Successive samples were withdrawn, as necessary, at intervals ranging from one-half to four hours. The samples were discharged into iodine flasks containing about 50 ml. of cold water to stop the reaction.

In runs in which the starting sulfamate and hydrogen ion concentrations were not equal, two initial samples were taken, one to be titrated for sulfamate content and the other with standard base for the initial hydrogen ion concentration.

Runs were made at 80.35, 90.00 and 98.00°, and at concentrations ranging from 0.005 to 0.04 molar in sulfamate ion. Depending upon the speed of the hydrolysis, the extents of reaction followed varied from 20 to 50%.

Results

Preliminary kinetic experiments showed that the hydrolysis proceeds as a first order reaction with respect to sulfamate and to hydrogen ions. If we designate the initial sulfamate and hydrogen ion concentrations by a and b , and the concentration of sulfamate decomposed at any time t by x , then the concentrations of sulfamate, hydrogen, ammonium, and bisulfate ions at time t will be, respectively, $a - x$, $b - x$, x and x . However, due to the dissociation of the bisulfate ion, hydrogen ions removed by reaction are partly regenerated. Hence the hydrogen ion concentration at time t is $b - x + y$, and that of the bisulfate ion is $x - y$, where y is the decrease in concentration of the bisulfate ion due to dissociation. We obtain thus for the over-all reaction and the concentrations of the various ions at time t



From expression (1), the rate of decomposition of the sulfamate ion follows as

$$dx/dt = k(a - x)(b - x + y) = k_0f(a - x)(b - x + y) \quad (2)$$