calcium chloride solution–ice, and finally a Dry Ice–acetone-bath.

Temperature measurements were made with a copper–constantan thermocouple by means of a Leeds and Northrup precision type potentiometer No. 7551. This instrument could be read to one microvolt corresponding to a temperature difference of approximately 0.02°.

The thermocouple was made from No. 32 B and S gage copper and constantan wires. To prevent contamination of the melt and also to provide good thermal contact, the junctions were enclosed in fine glass tubes about 5 mm. long which were collapsed tightly upon the metal.

The thermocouple was calibrated against the following accurately known transition points: melting point of tin (231.85°), boiling point of water, transition temperature of Glauber's salt (32.384°), and melting point of mercury (−38.89°).

Studies were made first on the indium-rich alloys. These were prepared by adding the desired increments of mercury to the previously analyzed alloys in a 15 × 120 mm. test-tube. In a similar manner mercury–rich alloys were prepared. The volume of sample analyzed was limited to about 5 ml. The alloys were covered with mineral oil to protect them from oxidation and wetting the walls of the tube. All samples were cooled from above the melting point of indium to at least −10°.

Results.—The results are given in Table I and are plotted in Fig. 1.

TABLE I

Sample	Weight % indium	Liquidus temp., °C.	Solidus temp., °C.
1	100.00	156.2	156.2
2	97.46	151.3	148.9
3	90.12	135.1	125.8
4	84.07	121.7	90.2
5	79.30	108.2	...
6	74.70	94.2	...
7	69.84	78.1	...
8	64.89	59.2	...
9	60.01	37.6	...
10	54.92	10.3	...
11	49.98	...	...
12	45.01	...	...
13	40.04	...	...
14	32.98	...	...
15	25.01	...	...
16	20.00	...	...
17	14.95	...	...
18	10.06	...	...
19	4.93	...	...
20	0.00	...	...

Between 10° and the melting point of indium, 156.2°, the solubility of indium in mercury is expressed by the equation

$$\log N_2 = (122.13/T) + 0.0027625T - 1.4740$$

where N_2 is the weight fraction indium and T is in °K.

Since these results differ seriously from those reported by Parks and Moran[5] the following supplementary experiment was performed. At room temperature (approximately 25°), weighed portions of indium and mercury were mixed to yield two mixtures, containing 84.4 and 63.2% mercury. In each case, within a few minutes the indium seemed to have dissolved to yield a homogeneous liquid. To ensure that a two-phase system was not formed each mixture was subjected to centrifugation and then separate portions of the alloy were analyzed as follows: A sample was removed from the top of each mixture and another from the bottom. Each was weighed and treated with hot concentrated hydrochloric acid to dissolve the indium. The mercury, which was unattacked by the acid, was dried and weighed. The composition of the upper and lower samples were found to be essentially the same and equal to that of the total mixture. (In the case of the mixture containing 63.2% Hg, the lower sample analyzed 62.9% and the upper 63.0%.)

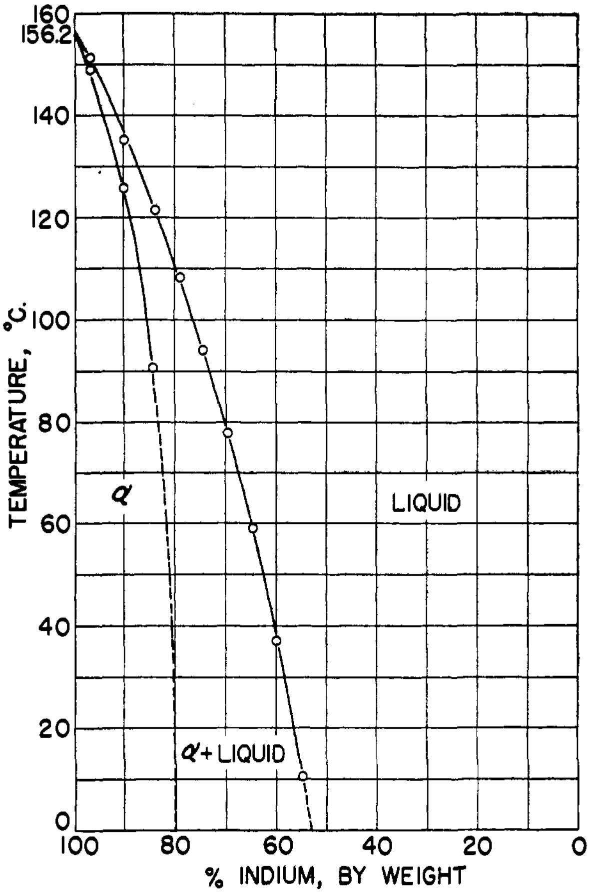

Fig. 1.

The cooling curves indicate that mercury forms a solid solution with indium. The solid solution region is labeled α in Fig. 1.

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The Logarithmic Growth Law for the Oxidation of Titanium

BY J. T. WABER, G. E. STURDY AND E. N. WISE

RECEIVED JUNE 2, 1952

Two different studies of the oxidation of titanium have led to contradictory interpretations regarding the form of the rate law above and below 350°. Gulbransen and Andrew[1] concluded that a modified parabolic rate law holds throughout the range 250 to 600°, although their Arrhenius plot of the parabolic rate constants shows a change of slope for

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[1] E. A. Gulbransen and K. Andrew, *J. Metals*, **1**, 741 (1949).

temperatures below 350°. Alexander and Pidgeon[2] obtained a logarithmic growth law in their study throughout the range 25 to 330°. However, above 460° both investigations established that oxidation was controlled by diffusion. The latter investigators state that the parabolic growth law was not applicable to their data.

According to Gulbransen and Andrew the energy of activation for temperatures above 350° is 26.0 kcal./g. mole of activated complex. The author's calculation from the slope at lower temperatures leads to 12.4 kcal./g. mole for this energy of activation. In a study of the oxidation of tantalum, the authors[3] observed a similar change in the energy of activation from 12.57 kcal./g. mole for the logarithmic growth law to 27.2 kcal./g. mole for the parabolic rate.

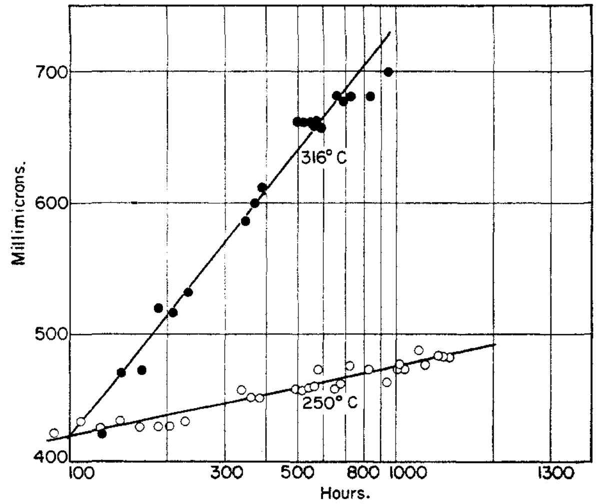
The present study was undertaken to determine whether the break in the Arrhenius plot of Gulbransen and Andrew's data is due to a change in the rate law. It was found that a logarithmic growth law represents the data up to 316°

$$\lambda = k_L \log(t + 1)$$

where λ is the wave length corresponding to maximum absorption after t hours of exposure. At this temperature, one run was observed to follow a cubic growth law.

Experimental Procedures.—Iodide titanium analyzing 500 p.p.m. of aluminum and 10 p.p.m. each of iron, silicon and magnesium was cold rolled without intervening anneals to 28 mil sheet specimens at Battelle Memorial Institute. These specimens were hand polished through 4/0 aloxite metallographic paper and then finished on dry gamal cloth without added abrasive.

The course of oxidation was followed spectrophotometrically as well as gravimetrically. The details of the two methods and evidence of the reliability of the former method have been presented elsewhere.[3,4]



OXIDATION OF TITANIUM.

Fig. 1.—A logarithmic plot of the spectrophotometric data obtained in the study of the oxidation of iodine titanium.

The specimens lost weight for about 50 hours, although the interference colors due to the oxide were present. These colors progressed smoothly, changing to those characteristic of greater oxide thicknesses with ensuing time. Repeated heating, followed by polishing to remove the oxide coating, reduced the magnitude and duration of the weight loss.

Alexander and Pidgeon[2] mention that their titanium, made by the Kroll–Dean method, contained about 0.05% hydrogen, which could only be partially removed by outgassing at 311°. The authors believe that the large weight decrease was probably a result of the escape of hydrogen.

Dr. Gulbransen kindly tested one of these samples in his vacuum microbalance. After the sample was outgassed in a high vacuum at 600°, there was a slight decrease in weight prior to oxidation but the behavior of this sample was then no different from that of outgassed specimens which he had discussed earlier in his paper with Andrew.

Experimental Results.—The spectrophotometric data are summarized in Fig. 1. Fairly consistent data were obtained both at 250 and 316°. The ordinate plotted is the wave length of the light which at each time corresponded to the minimum on the reflectance curve. The present data are too few to permit accurate determination of the activation energy, ΔE, in the lower temperature range. However, a preliminary estimate of this quantity based upon the rate constant, k_L, indicates that it is of the order of 13 kcal./g. môle. The values from which it was estimated are given in terms of ångströms in Table I.

TABLE I

VALUES OF THE LOGARITHMIC RATE CONSTANT FROM THE SPECTROPHOTOMETRIC DATA

Temp., °C.	k_L in Å.	
250	507	520
316	3350	5700

Conclusions.—The oxidation of titanium below 350° has been reinvestigated and found to follow the logarithmic growth law, confirming the work of Alexander and Pidgeon. The break in the Arrhenius plot of Gulbransen and Andrew is due to the change from the logarithmic to the parabolic rate law at temperatures increasing above 350°.

Acknowledgments.—The assistance of C. R. Tipton in procuring the cold-rolled specimens is acknowledged. Discussions with F. W. Schonfeld, A. S. Coffinberry and E. R. Jette were helpful and the kind counsel of E. A. Gulbransen was greatly appreciated.

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[2] W. A. Alexander and L. M. Pidgeon, *Can. J. Research*, **28B**, (1949).

[3] J. T. Waber, E. N. Wise, G. E. Sturdy and C. R. Tipton, *J. Electrochem. Soc.*, **99**, 121 (1952).

[4] It should be pointed out that small thicknesses of lower oxides may increase the phase shift in terms of equivalent oxide thickness although the fundamental equations of the spectrophotometric method are not changed. It has been assumed that lower oxides of titanium were not present in significant amounts.

Studies in the Furan Series. Reaction of Some Substituted 2-Furamides with Phenyl Isocyanate

BY JOE R. WILLARD AND CLIFF S. HAMILTON

RECEIVED DECEMBER 13, 1952

In conjunction with other studies in the furan series, some 5-substituted-2-furamides were treated with phenyl isocyanate according to the procedure of Wiley[1] to give the corresponding 1-(5-substituted-2-furoyl)-3-phenylureas. To show that normal addition had occurred, 1-(2-furoyl)- and 1-(5-bromo-2-furoyl)-3-phenylurea were prepared by reaction of phenylurea with the corresponding furoyl chloride according to the method of Stoughton.[2] In accord with the observations of Wiley,[1b]

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[1] (a) P. F. Wiley, THIS JOURNAL, **71**, 1310 (1949); (b) **71**, 3746 (1949).

[2] R. W. Stoughton, *J. Org. Chem.*, **2**, 514 (1938).