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Uranium Compatibility Studies

Part 1: The Interaction of Uranium with Gas Free Water
and Water Vapour

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Part 1. The Interaction of Uranium with Gas Free Water and Water Vapour

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Summary

The interaction between uranium and both liquid water and water vapour has been studied in the absence of permanent gases in the temperature range 35° - 100°C. The reaction has been shown to proceed at a uniform rate dependent on the temperature and available uranium surface area. The reaction mechanism appears to be unchanged in the temperature range investigated.

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1. INTRODUCTION

A consideration of the factors governing the compatibility of uranium with polymeric organic materials revealed that the chemical affinity of the metal for water vapour would have a profound effect on the results of any experimental evaluations. A literature survey revealed that while a considerable amount of work has been reported on the corrosion of uranium at elevated temperatures (400° - 1000°C) relatively little quantitative work has been carried out on the uranium-water reaction at temperatures below 100°C. However it has been established that gases affect the rates of the uranium-water and the uranium-water vapour reactions and it is claimed that oxygen inhibits the reaction while hydrogen causes acceleration [1,2]. No report could be found of a quantitative study of the reaction between uranium and gas free water vapour involving both products and rates of reaction over the temperature range 0° - 100°C. The results of such a study would form the basis for the determination of the relative compatibility of other materials and hence it was decided to commence the work by an investigation into the uranium-water vapour reaction.

2. EXPERIMENTAL

2.1 Materials

The uranium used was all magnesium reduced unadjusted natural metal in the form of rods having a surface area of 0.3372 cm²/cm of length. The material was supplied in the form of wire which had been hot extruded in the γ phase. The major impurities present in the metal are outlined in Table 1.

TABLE 1

Quantities of Impurities Present in Uranium

Metal Used

Material	p.p.m.
Iron	98
Silicon	17
Aluminium	15
Carbon	150

2.2 Experimental Procedure

As outlined in the Introduction it was desired to investigate the reaction of uranium with gas free water vapour, a literature survey indicating that oxygen was the most important gas to exclude. It has been suggested that the standard freeze-melt technique for the de-aeration of aqueous solutions may leave some residual oxygen in the system [3] and hence an attempt was made to remove most of the oxygen using the following method, before evacuation.

A sample of distilled water (~ 25 ml) was introduced into a small standard distillation apparatus and nitrogen gas (BOC white spot) was bubbled through the water for a period of about 30 min. The water was then distilled under reduced pressure (water pump) with a nitrogen leak and the gas passed through the apparatus until the water was required (within 1 h of distillation).

For reactions involving water vapour, 100 μ l of the nitrogen distilled water together with a uranium rod were placed in a specially adapted break-seal ampoule (Figure 1) and the water was degassed at 10^{-6} torr by the standard freeze-melt technique. For water immersion experiments 3 ml of the nitrogen distilled water were introduced into a normal break-seal ampoule containing a uranium rod and degassed in the same manner. The evacuated ampoules were sealed with an oxygen gas flame and exposed for a predetermined time, in a thermostated oil bath maintained at $\pm 0.5^{\circ}\text{C}$ of the required temperature. The exposed ampoules were removed, in triplicate, from the oil bath at regular time intervals, opened on a vacuum line to remove gaseous products and the corroded uranium rod treated with nitric acid to remove quantitatively the reaction products.

Before exposing to water or water vapour the uranium rods were immersed in nitric acid (density 1.420 g cm^{-3}) until clean, then successively washed in water and acetone, dried and finally weighed. At the completion of the experiment the corroded rods were similarly immersed in nitric acid for 1 min only, then washed, dried and weighed as previously described. The apparent weight loss during exposure thus recorded was in excess of the actual value by the quantity of uranium metal consumed during the 1 min immersion in the nitric acid. To correct for this the cleaned weighed rod was reimmersed for a further minute in the acid bath and the weight loss during the second immersion subtracted from the apparent weight loss during exposure. For the length of rod used in these experiments (2 cm) the correction factor was very small ($3 - 5 \times 10^{-5}$ g) and was usually less than 1% of the corrected corrosion weight loss. A period of 1 min was originally chosen as the standard acid immersion time since preliminary experiments had revealed that the oxidation products could be removed from a corroded uranium specimen in 10 to 30 s of acid immersion. The standard time therefore ensured complete removal of the corrosion products during the first acid treatment. Preliminary experiments also revealed that the correction factor remained the same whether determined before or after exposure provided that the geometric area of the uranium specimen remained sensibly unaltered during the experiment.

3. RESULTS

3.1 Results in the Presence of Water Vapour

The results obtained from exposure of uranium to gas free vapour at temperatures of 35° , 50° , 65° , 80° and 100°C , and the corrosion rates obtained from graphical interpretation of these results are given in Table 2.

TABLE 2

Temperature, °C	Exposure Period, h	Uranium Reacted, mg		
35	120	1.6	4.9	3.0
	235	10	7.7	8.0
	360	11	12	11
	480	18	18	20
	693	28	28	28
	720	30	32	31
	840	36	37	36
	Observed Oxidation Rate 0.060 mg cm⁻² h⁻¹			
50	80	3.0	2.9	-
	162	39.2	39.0	-
	257	46.0	40.2	-
	380	54.8	54.3	-
	429	62.2	60.1	-
	480	63.5	64.8	-
	555	77.6	78.2	-
	640	90.2	99.0	-
	710	101	-	-
	800	115.2	115.5	-
Observed Oxidation Rate 0.21 mg cm⁻² h⁻¹				
65	74	22	22	29
	162	83	83	-
	235	94	94	95
	320	107	116	97
	400	147	170	159
	480	183	176	162
	645	243	242	242
	716	238	266	248
	Observed Oxidation Rate 0.679 mg cm⁻² h⁻¹			
80	48	45	46	46
	96	96	99	93
	144	138	139	137
	190	185	184	183
	261	231	231	231
	290	245	244	245
	338	273	273	277
	384	281	281	281
	408	287	289	288
	480	307	311	-
Observed Oxidation Rate 1.742 mg cm⁻² h⁻¹				
100	4	7.6	9.1	10
	8	23	23	24
	17	66	53	46
	24	80	84	88
	28	99	82	-
	41	132	148	-
	48	157	141	156
	56	172	182	-
Observed Oxidation Rate 4.75 mg cm⁻² h⁻¹				

A graphical interpretation of these results is illustrated in Figure 2, reference to the figure reveals that while straight line plots have been obtained for four of the temperatures investigated, one (80°C) yielded a straight portion succeeded by a curve. The conditions of the experiment at 80°C were such that at 480 h exposure 96 - 98% of the uranium had been oxidised and thus a rate expressed in the units $\text{mg cm}^{-2} \text{h}^{-1}$ would not be constant since the area would change appreciably. The initial radius of the uranium rod was 0.0523 cm and the mean radius of two rods after 480 h exposure was 0.010 cm (variation along the rods between 0.008 to 0.011 cm). It has been calculated from the assumption of uniform attack on the whole uranium surface (Appendix) that the final radius after 480 h exposure would be 0.011 cm which compares most favourably with the observed result (0.010 cm). Straight line plots were obtained for reactions at the other temperatures because considerably less uranium was oxidised during the course of the experiments.

3.2 Results of Water Immersion Experiments

These experiments were performed at temperatures of 35°, 65° and 80°C and the results are given in Table 3.

TABLE 3

Temperature, °C	Exposure Period, h	Uranium Reacted, mg		
35	138	2.8	3.1	1.0
	240	6.1	6.2	5.7
	360	11	11	12
	483	16	14	15
	605	17	18	18
	720	32	31	28
	955	33	34	32
	1076	40	38	41
	1200	41	42	42
	Observed Oxidation Rate $0.071 \text{ mg cm}^{-2} \text{h}^{-1}$			
65	96	39	43	43
	167	49	53	54
	236	89	90	86
	314	117	126	125
	410	144	149	138
	480	157	161	156
	552	187	193	195
Observed Oxidation Rate $0.63 \text{ mg cm}^{-2} \text{h}^{-1}$				
80	24	19	27	19
	48	38	38	-
	72	75	84	59
	96	88	81	108
	120	101	117	-
	144	134	127	140
	160	159	157	151
	186	172	172	174
	216	194	193	193
	Observed Oxidation Rate $1.75 \text{ mg cm}^{-2} \text{h}^{-1}$			

A graphical interpretation of these results is illustrated in Figure 3, straight line plots have been obtained for each of the three temperatures.

4. DISCUSSION

From the results given in the previous section it is apparent that under the conditions of the experiments linear corrosion rates are exhibited over the temperature range examined. It is well documented that the major products of the reaction between uranium and water vapour are hydrogen and uranium oxides [4 - 6]. Since no attempt was made to remove these reaction products it may be assumed from the rate studies that the reaction is not autocatalytic.

It has been observed [4] that the reaction rate at various temperatures for the aqueous corrosion of uranium can be correlated by the Arrhenius equation

$$K = A e^{-\frac{E}{RT}}$$

where K = observed reaction rate,
 A = the frequency factor of the reaction,
 E = the energy of activation,
 R = the molar gas constant = 1.98 cal mol⁻¹,
 and T = the temperature in degrees Kelvin,

This equation may be rewritten in the form

$$\log_{10} K = \log_{10} A - \frac{E}{2.303RT}$$

Thus a plot of $\log_{10} K$ against $\frac{1}{T}$ should yield a straight line of gradient $\frac{E}{2.303R}$

Figure 4 shows an Arrhenius plot of this form for the results given in Table 2. A good straight line has been obtained and the activation energy, determined from the gradient, has the value 16.1 kcal mol⁻¹.

The usual form of the Arrhenius equation used for surface reactions is

$$K = kC = A e^{-\frac{E}{RT}} C,$$

where K = observed reaction rate, as above,
 k = the reaction rate constant = $A e^{-\frac{E}{RT}}$,
 C = the concentration of adsorbed water.

$$\text{Hence } k = \frac{K}{C} = A e^{-\frac{E}{RT}}.$$

In this form the log of the rate constant is plotted against the reciprocal of the temperature. The rate constant is determined by dividing the observed reaction rate by the concentration term. The concentration of adsorbed water

will be dependent on the vapour pressure at the reaction temperature,

$$\text{i.e., } C = b P,$$

where b = a combination of constants related to the entropy and surface energy of adsorption,

and P = the vapour pressure of the water at the reaction temperature.

$$\text{Thus } k = \frac{K}{b P} = A e^{-\frac{E}{RT}},$$
$$\text{hence } \frac{K}{P} = A b e^{-\frac{E}{RT}}$$

Thus it may be considered that if the reaction is first order with respect to water vapour a plot of $\log_{10} \frac{K}{P}$ against $\frac{1}{T}$ should yield a straight line. This plot is illustrated in Figure 5 and a straight line has been obtained.

However further consideration reveals that the variation of water vapour pressure with temperature has the same exponential form as the variation of rate constant with temperature and this is confirmed over the temperature range under investigation by the graph illustrated in Figure 6. From these considerations it may be seen that the straight line obtained by plotting

$\log_{10} \frac{K}{P}$ against $\frac{1}{T}$ has no significance since P is an exponential function of T

(i.e., $P = P_0 e^{-\frac{X}{T}}$). Thus further work is necessary to determine whether or not the reaction rate is dependent on the vapour pressure of the water. Until such results are available it may be assumed that the reaction is of zero order and the plot of $\log_{10} K$ against $\frac{1}{T}$ is therefore admissible. Some support

is lent to this proposal by the fact that observed reaction rates in water immersion conditions are identical to those obtained under saturated vapour conditions at the same temperature.

5. CONCLUSIONS

From the results presented herein it may be concluded that in the absence of permanent gases the reaction between uranium metal and water vapour is not autocatalytic and no change in rate is observed on passing from saturated vapour to water immersion conditions. The reaction has been shown to be fairly uniform over the whole uranium surface and while a surface roughening undoubtedly occurs no deep pitting has been observed. The Arrhenius plot for the temperature range 35° - 100°C is a good straight line and thus it may be concluded that the reaction mechanism is unchanged up to 100°C, hence accelerated tests are justified and may be interpolated for lower temperature conditions.

6. FURTHER WORK

Work is now in hand to determine the effect of vapour pressure on the rate of reaction between uranium and water vapour in the absence of permanent gases and the effect of permanent gases on the reaction rate is also being investigated. A further study is directed at the elucidation of the reaction products formed both in the presence and absence of permanent gases. The results of these studies will be presented in due course.

7. ACKNOWLEDGEMENTS

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APPENDIX

THE EFFECT OF THE AREA OF A URANIUM ROD ON ITS CORROSION RATE

In the following calculations three basic assumptions have been made:-

- (a) The rate of reaction is initially linear.
- (b) The corrosion is uniform over the whole cylindrical surface of the rod.
- (c) The surface area of the rod remains sensibly unaltered during the time intervals considered (~ 48 h).

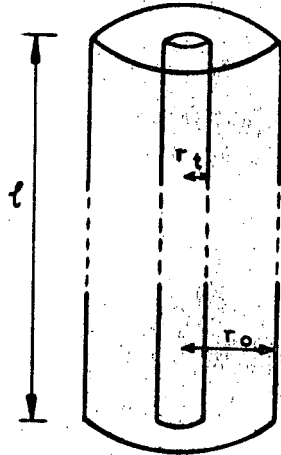


FIGURE A1

Considering a rod of uranium as shown above, where l is the length of the rod in cm. (This remained unchanged during exposure),

- r_0 the initial radius of the rod in cm,
- A the initial area of the rod in cm^2 ,
- ρ the density of uranium in mg cm^{-3} ,
- r_t the radius in cm after t h exposure,
- R the initial rate of corrosion in $\text{mg cm}^{-2} \text{h}^{-1}$.

The initial rate of uranium consumption = $RA \text{ mg h}^{-1}$.

Hence after t h quantity consumed = $RA t \text{ mg}$.

Thus volume of metal consumed = $\frac{RA t}{\rho} \text{ cm}^3$ (1)

The initial volume of the rod = $\pi r_0^2 l$

The volume of the rod after t h exposure = $\pi r_t^2 l$

Hence volume of metal consumed = $\pi r_0^2 l - \pi r_t^2 l$ (2)

Combining (1) and (2)

$$\pi r_0^2 l - \pi r_t^2 l = \frac{RA t}{\rho}$$

$$\text{i.e., } l\pi\rho(r_0^2 - r_t^2) = RA t,$$

$$\text{hence } r_t^2 = r_0^2 - \frac{RA t}{l\pi\rho},$$

$$\therefore r_t = \sqrt{r_0^2 - \frac{RA t}{l\pi\rho}}$$

Using the derived formula, r_t and hence A_t may be calculated for each time interval, where A_t is the area of the rod after t h exposure. The value A_t may then be considered as the initial area for the next time interval t hours. Using this technique, for time intervals of approximately 48 h, the radius of the rod after 480 h may be calculated and compared with the experimentally derived value. These calculations are outlined in Table A1.

TABLE A1

Exposure Time, T	Time Interval, t	tR	tRA	$\frac{tRA}{l\pi\rho}$	$r_0^2 - \frac{RA t}{l\pi\rho}$	r_t	A_t
48	48	69.792	47.0398	0.0004004	0.002335	0.04832	0.6219
96	48	69.792	43.4036	0.0003694	0.001966	0.04434	0.5695
144	48	69.792	39.7479	0.0003383	0.001628	0.04035	0.5172
190	46	66.884	34.5924	0.0002944	0.001334	0.03652	0.4673
261	71	103.234	48.2412	0.0004106	0.000923	0.03039	0.3877
290	29	42.166	16.3465	0.0001391	0.0007839	0.02800	0.3568
333	48	69.792	24.9018	0.0002119	0.0005720	0.02392	0.3042
384	46	66.884	20.3461	0.0001732	0.0003988	0.01997	0.2635
408	24	34.896	9.1951	0.0000783	0.0003205	0.01789	0.2269
480	72	104.688	23.7537	0.0002022	0.0001183	0.01088	0.1368

The initial values used in the calculations were

$$l = 2 \text{ cm} \quad A = 0.6744 \text{ cm}^2 \quad \rho = 18700 \text{ mg cm}^{-3}$$

$$R = 1.42 \text{ mg cm}^{-2} \text{ h}^{-1} \text{ (From first 48 h determination)}$$

$$r_0 = 0.0523 \text{ cm.}$$

The measured radius after 480 h exposure was 0.010 cm.
Calculated value from Table A1, 0.011 cm.

The results given in Table 2 for the observed oxidation of uranium at 80°C

may be corrected, by making due allowance for the area change occurring during the oxidation reaction. The area of rod during each time interval was taken to be the average of the calculated values for that area at the beginning and end of the interval. The corrected values of corrosion against time of exposure are given in Table A2.

TABLE A2

Exposure Time, T	Observed Weight Change, W, mg	Weight Difference ΔW , mg	Average Area, cm^2	$\frac{\Delta W}{A_v}$	$\sum \frac{\Delta W}{A_v}$
48	45.9	45.9	0.6479	73.0	73.0
96	96.1	50.2	0.6157	81.5	154.5
144	138.1	42.0	0.5431	77.5	232.0
190	183.8	45.7	0.4922	92.9	324.9
261	230.8	47.0	0.4275	110.0	434.9
290	244.8	14.0	0.3722	37.6	472.5
338	274.3	29.5	0.3305	89.3	562.8
384	280.9	6.6	0.2838	23.3	586.1
408	288.1	7.2	0.2452	29.4	615.5
480	309.3	21.2	0.1818	116	731.5

The values in the final column ($\sum \frac{\Delta W}{A_v}$) of Table A2 represent the quantity of uranium which would be oxidised if a rod of 1 cm^2 surface area were exposed to gas free water vapour at 80°C and the surface area remained unchanged as the reaction proceeded. A graphical interpretation of these results is illustrated in Figure 7, a linear plot was obtained and the oxidation rate determined was $1.65 \text{ mg cm}^{-2} \text{ h}^{-1}$, this value agrees extremely well with that obtained by considering only the early values of the uncorrected results ($1.74 \text{ mg cm}^{-2} \text{ h}^{-1}$).

These results indicate that the assumptions made concerning the rate and uniformity of the reaction were valid and that a pitting-type attack does not occur. However since the reaction rate was linear for approximately 200 h, on the uncorrected values and that during this time the percentage area decrease was of the order of 30% it necessarily follows that an increase in surface roughness resulted from the corrosion. Thus it may be concluded that a surface roughening but no deep pitting occurs during the reaction under the conditions of experimentation. The two photographs in Figure 8 illustrate the lack of pitting even after extensive corrosion has occurred. The uniformity of attack over the whole surface is illustrated by the photographs in Figure 9, the rods were supplied with a twist as shown, and the geometrical shape remained unchanged after exposure at 80°C .

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Ampoule was modified as shown, by introduction of small bulb connected to the ampoule by capillary tubing. The water was frozen into the small bulb and degassed before exposure. The uranium rod was exposed to water vapour alone and not to liquid water.

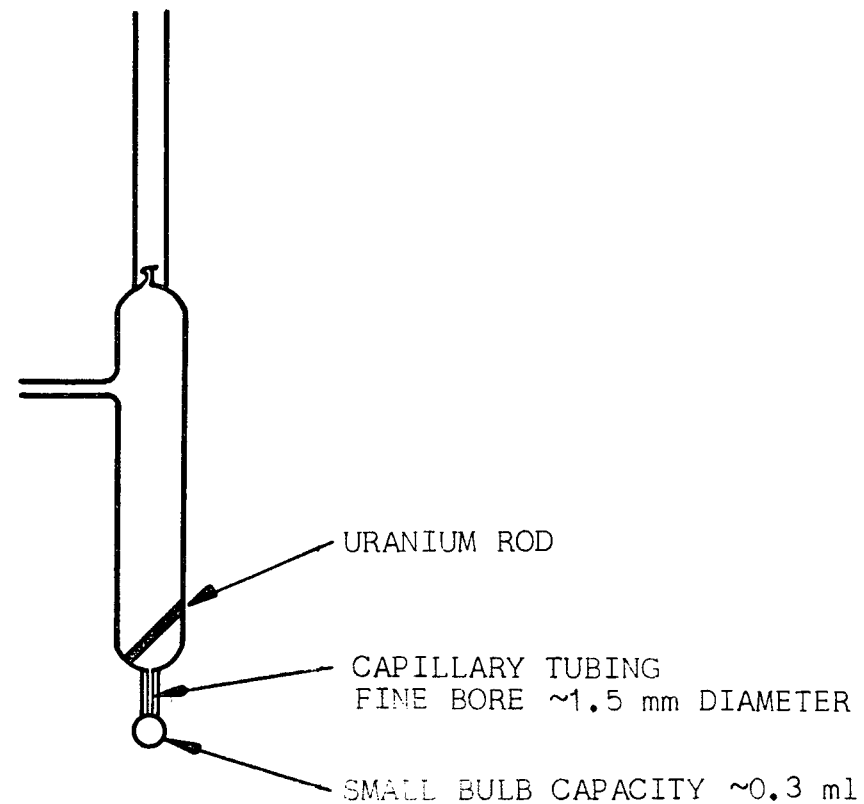


FIGURE 1. ADAPTED BREAK-SEAL AMPOULE

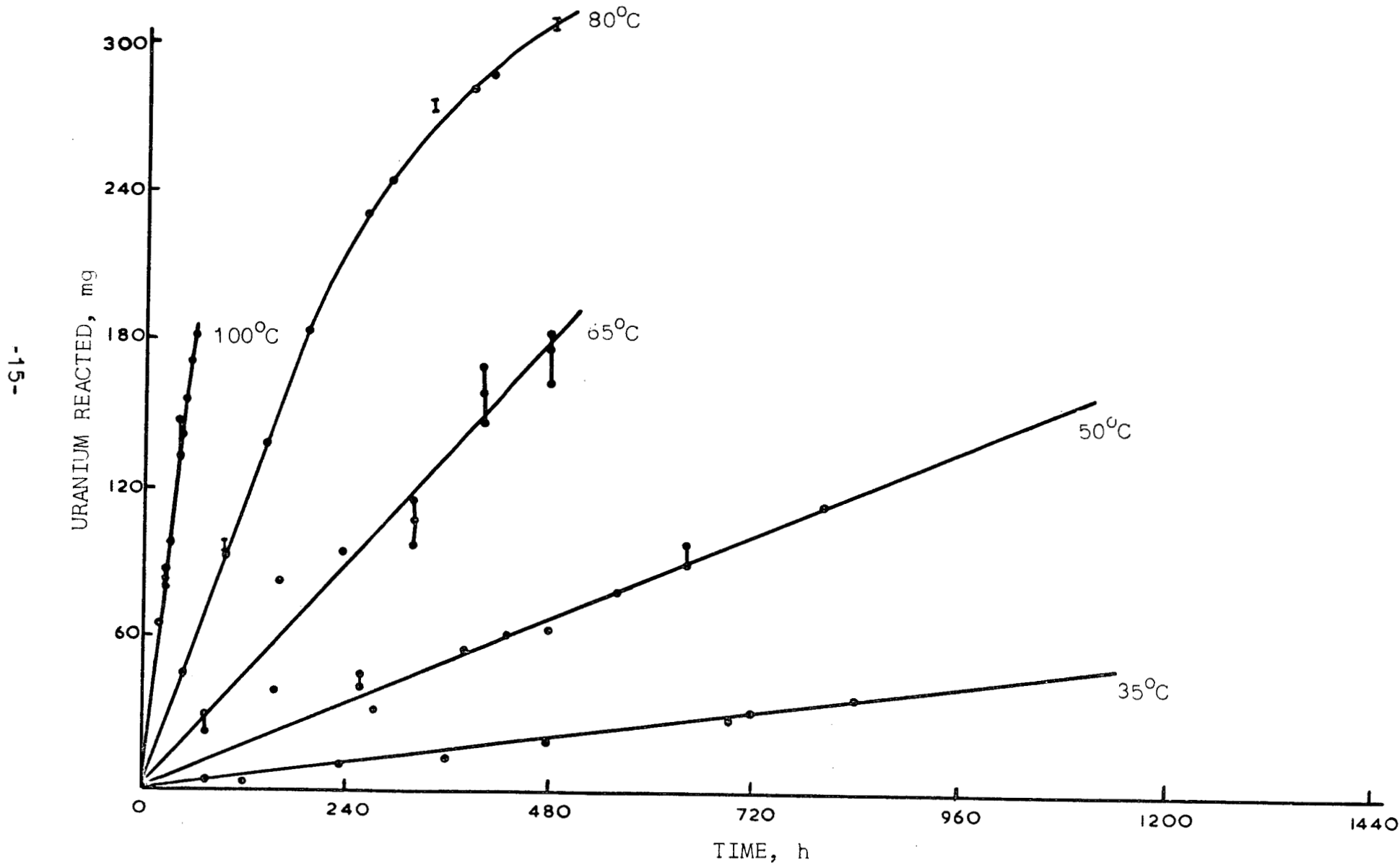


FIGURE 2. URANIUM IN CONTACT WITH GAS FREE WATER VAPOUR

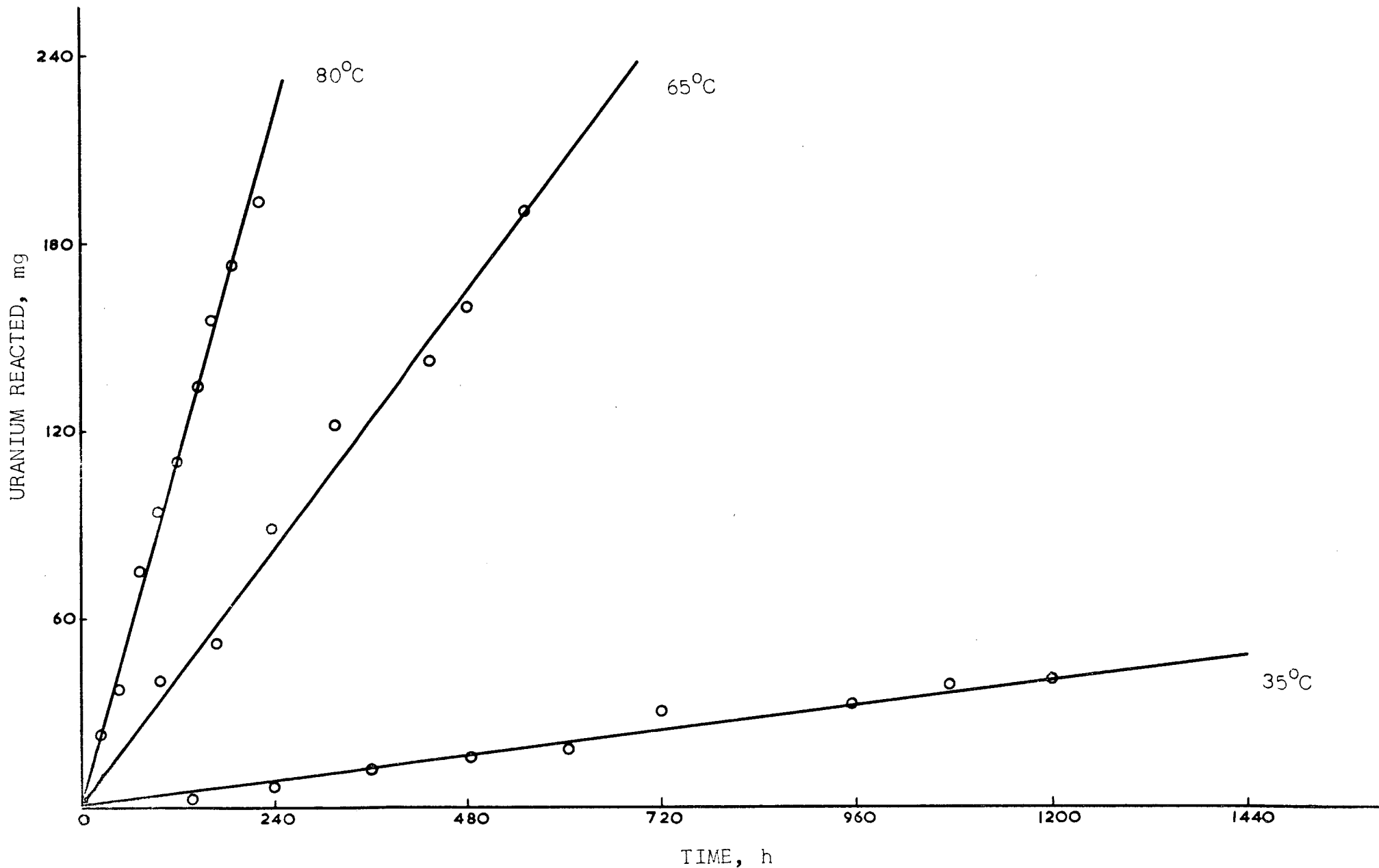


FIGURE 3. URANIUM IN CONTACT WITH GAS FREE WATER (IMMERSION CONDITIONS)

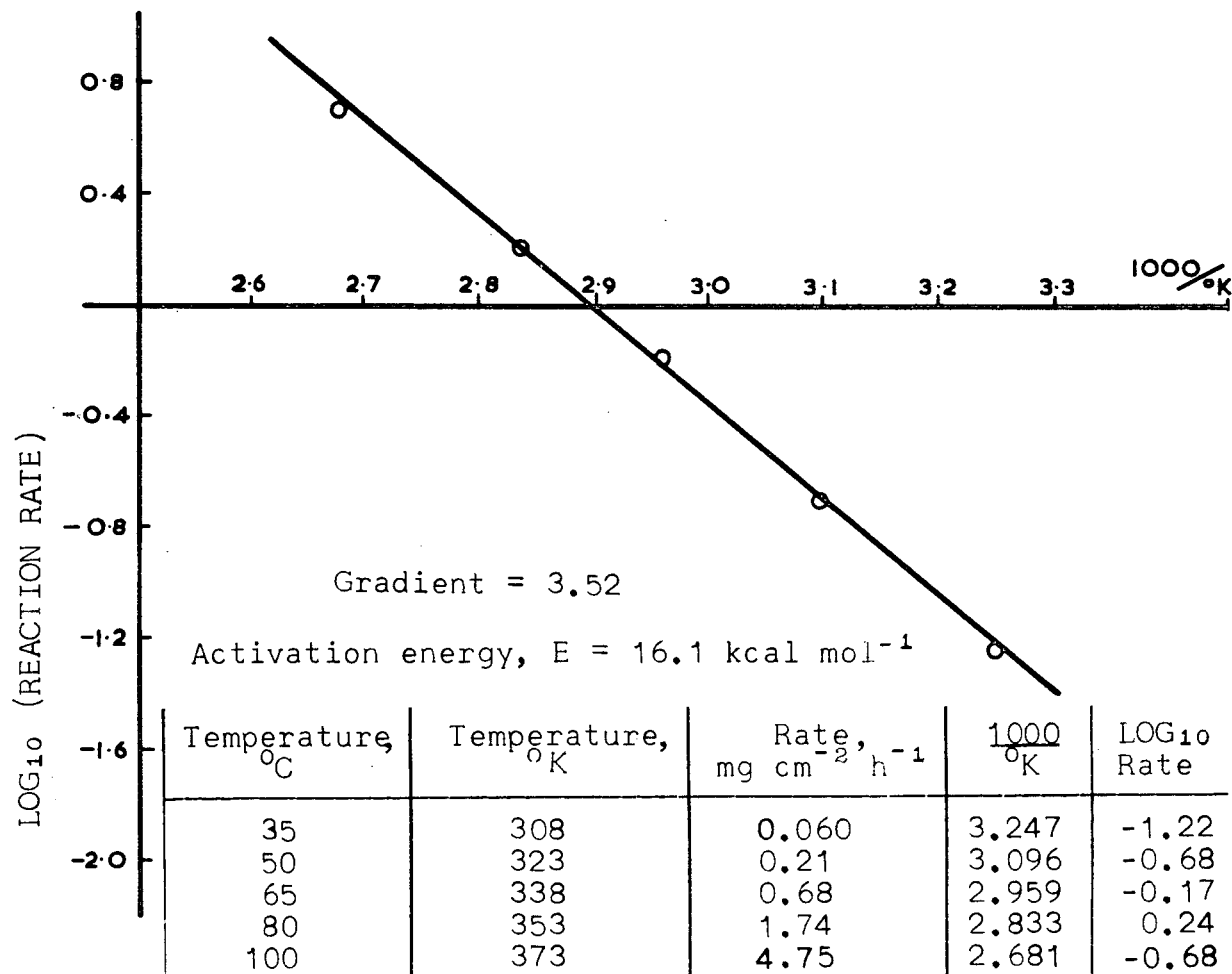


FIGURE 4. ARRHENIUS PLOT FOR ZERO ORDER REACTION

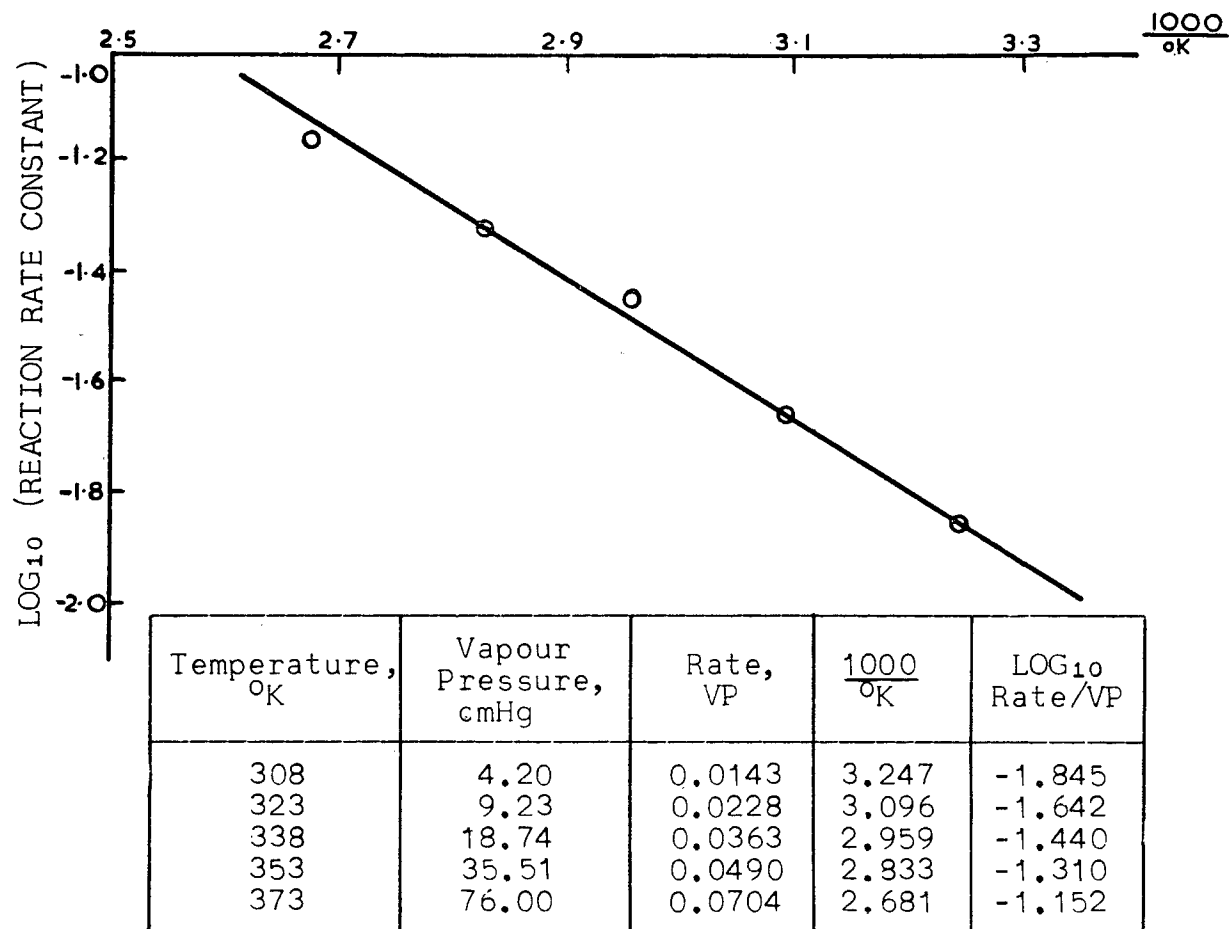
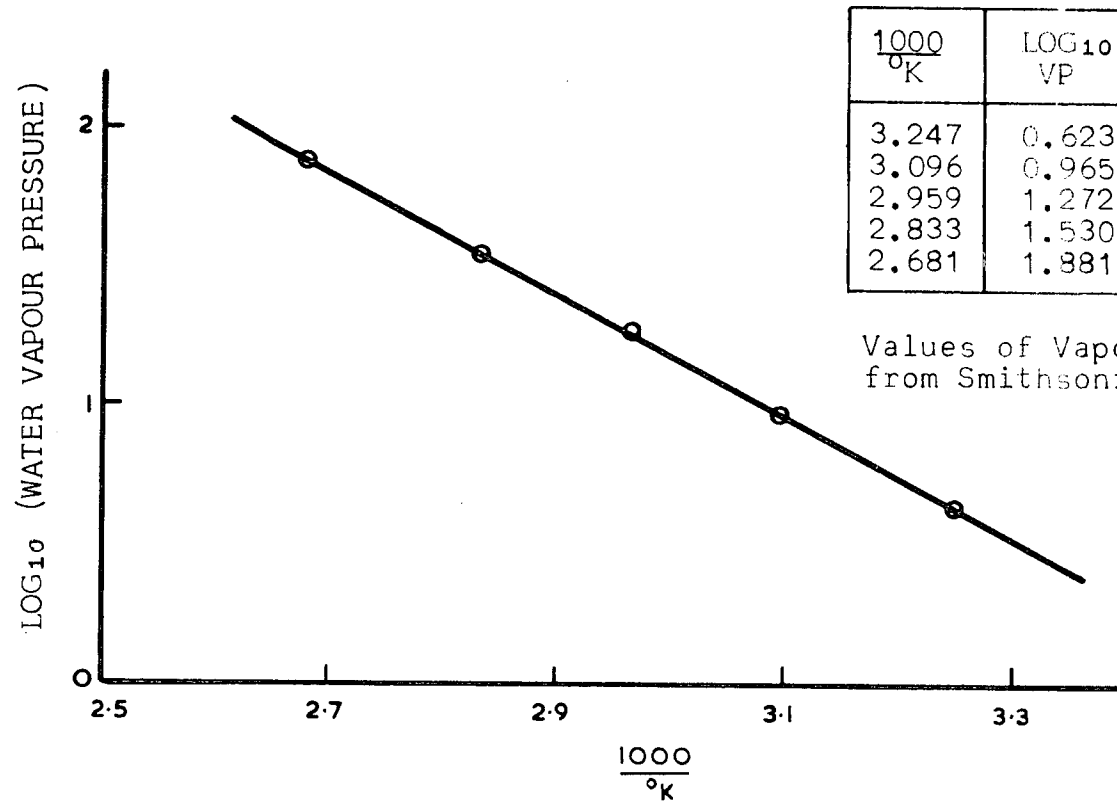


FIGURE 5



Values of Vapour Pressure taken from Smithsonian Physical Tables

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FIGURE 6. SHOWING EXPONENTIAL RELATIONSHIP BETWEEN WATER VAPOUR PRESSURE AND TEMPERATURE

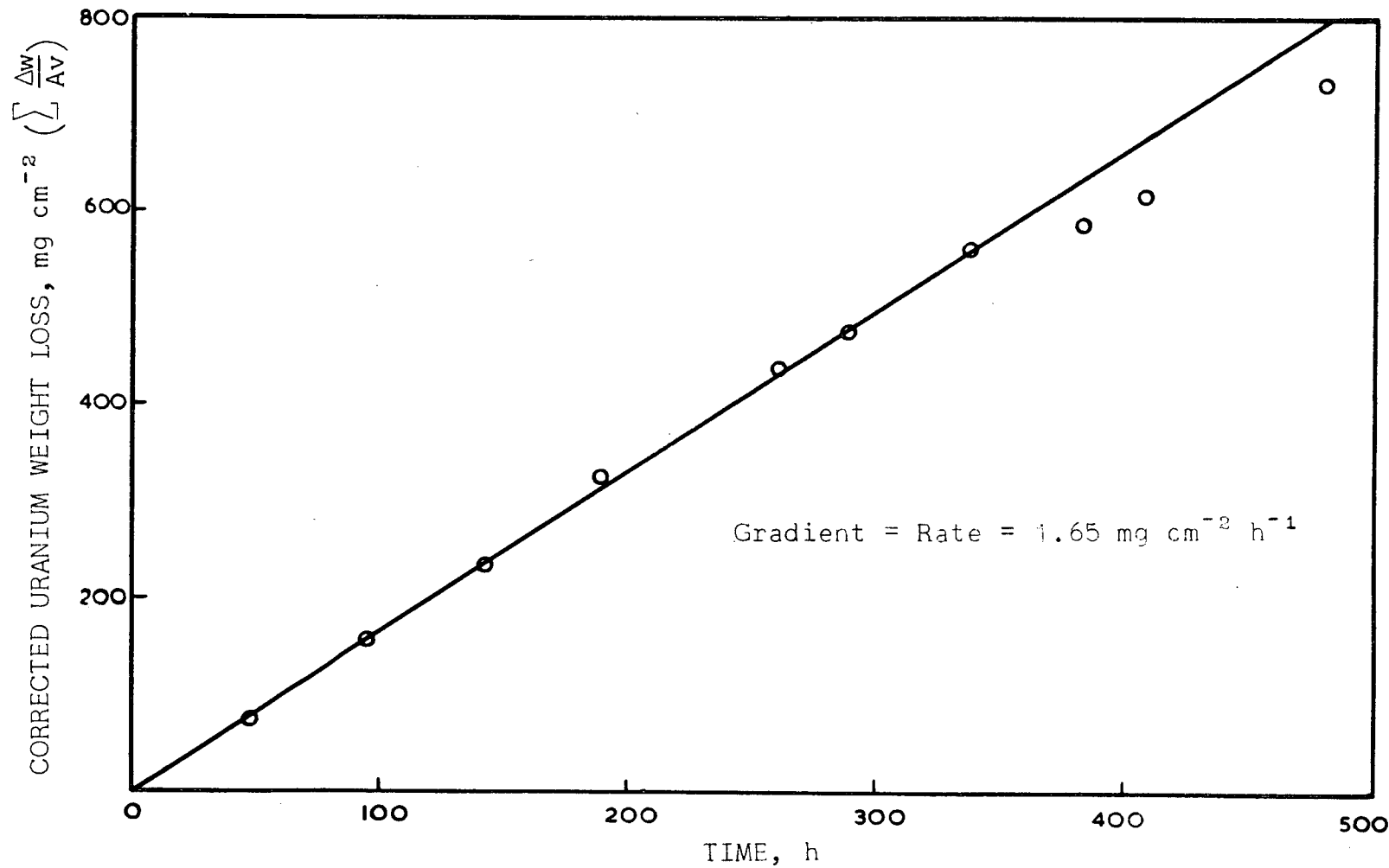


FIGURE 7

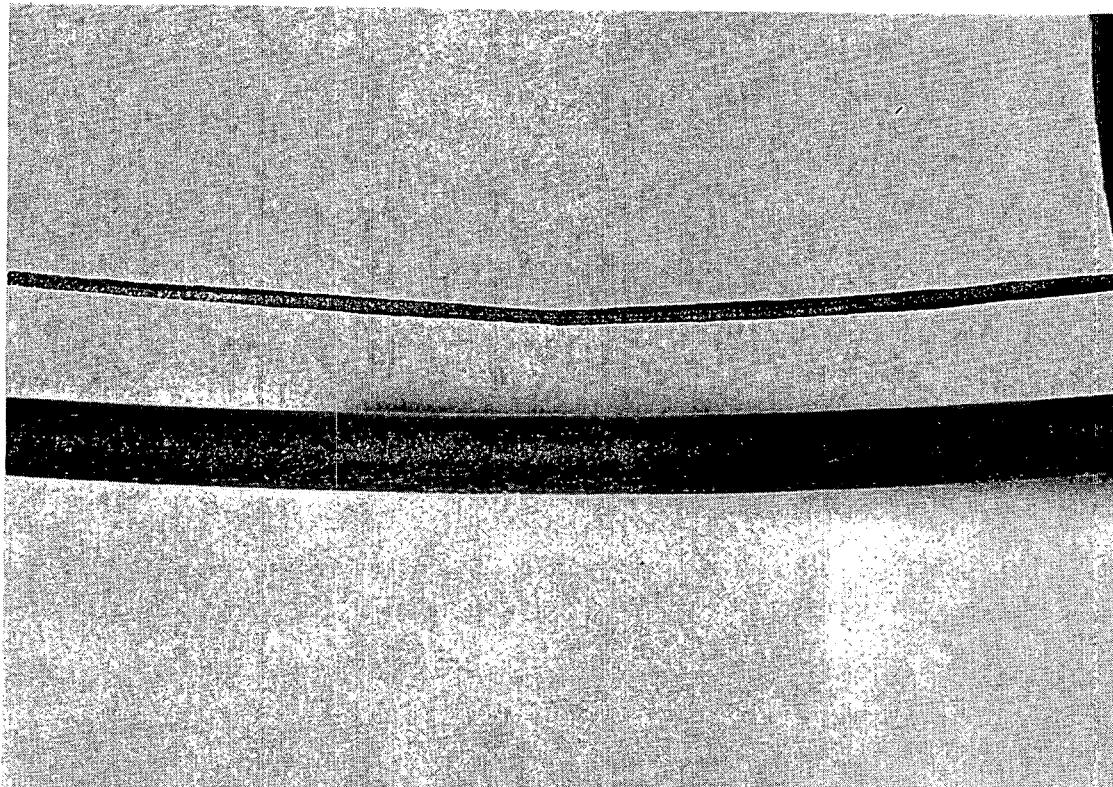


FIGURE 8

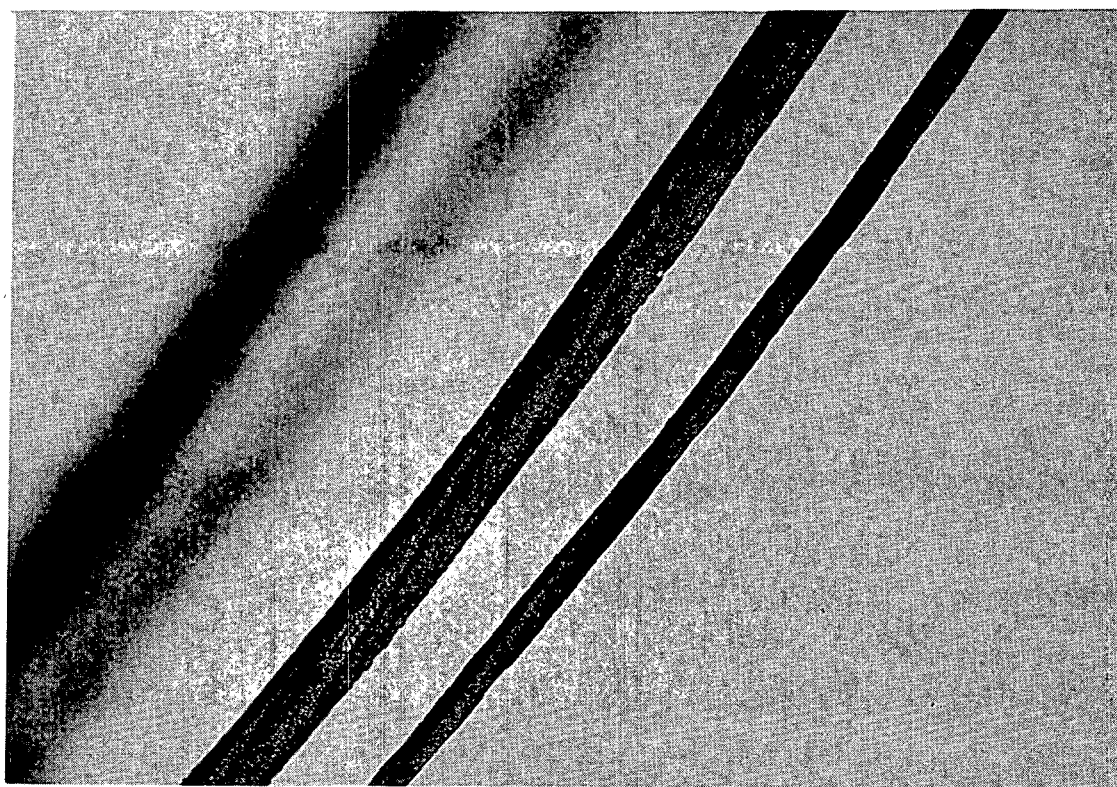


FIGURE 9

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