

KINETICS OF ISOTHERMAL ANNEALING OF RADIATION DAMAGE IN SZILARD-CHALMERS REACTION WITH COBALT COMPLEXES

Part I. Tris-Acetylacetonate Cobalt (III)—Section 1

BY AMAR NATH, K. S. VENKATESWARLU AND JAGDISH SHANKAR

(Atomic Energy Establishment, Trombay, Bombay)

Received January 21, 1957

(Communicated by Dr. H. J. Bhabha, F.R.S., F.A.Sc.)

INTRODUCTION

It has been observed earlier that the retention* of several neutron irradiated oxyanions¹⁻⁶ show an increase on subsequent heating. The kinetics of the process has been studied by heating samples of the irradiated compounds for known periods of time at fixed temperatures and an attempt made to analyse the data, but it was not found to obey any simple chemical rate law. Herr¹³ investigated in some detail the thermal annealing of the neutron irradiated K_2ReCl_6 crystals. Zuber⁷ showed that the data for tris-ethylenediamine Co (III) nitrate admitted of graphical analysis to yield two specific first-order reaction rates associated with two different activation energies.

The present paper forms part of a general comprehensive study of the thermal and radiation annealing of several irradiated cobalt complexes, which is ultimately expected to give some insight into the nature of the damage centres resulting from Szilard-Chalmers effect and other extraneous radiations. It has been found that the retention reaches a maximum characteristic of the temperature of annealing. For each temperature studied thermal annealing has been shown to follow first-order kinetics. The results of two-stage and multistage experiments show that the thermal history has a profound influence on the annealing behaviour.

EXPERIMENTAL

Preparation of tris-acetylacetonate cobalt (III).—It was prepared after Gach.⁸ All the chemicals used were either G. R. or extra pure grades of E. Merck. M.P. 198° C. (*cf.* West¹² 196° C. uncorrected).

* Of the atoms undergoing a nuclear transformation, that fraction which remains in, or reverts to, its initial molecular condition is called 'retention'.

Analysis	Found	Calculated for (C ₅ H ₇ O ₂) ₃ Co
Co	16.60	16.57%
C	50.56 50.64	50.6%
H	6.07 6.01	5.9%

Neutron irradiation.—Bulk quantities of the complex powder were irradiated in BEPO, Harwell, with a total integrated flux of the order of 2×10^{16} nvt. thermal neutrons and more than 10^6 roentgen of γ -radiation. It was stored at room temperature for about 2 years before the work reported here was commenced.

Heating and chemical separation.—Powder aliquots were drawn from the bulk irradiated sample and were maintained at specified temperatures for different periods of time in stoppered conical flasks in an electric air oven kept constant to within $\pm 0.5^\circ$ C. or in an oil-bath kept to within $\pm 0.2^\circ$ C. In the latter case, at the end of the heating period, the flask was chilled in cooled acetone to freeze the reaction.

Each aliquot was dissolved in about 15 ml. of benzene and the solution was transferred to a separating funnel. The flask was rinsed repeatedly with small amounts of benzene and the rinsings were transferred to the separating funnel. Eight to 10 ml. of an aqueous solution containing 3% EDTA (disodium salt) and 1% sodium-potassium tartrate and small amounts of cobalt sulphate (30–60 mg.) were added to the conical flask and then transferred to the separating funnel and struck with the benzene solution of the complex. The aqueous fraction was collected in a volumetric flask. The benzene fraction was struck successively with three aliquots of 8–10 c.c. 3% EDTA—1% tartrate solution, each time the solution being used first to rinse the conical flask to ensure its complete decontamination. The flask and the final fraction of the EDTA solution used for striking the complex were checked for the absence of activity using a probe monitor.

The aqueous extracts and the benzene fraction were both made up to the same volume with water and benzene respectively. Aliquots from these solutions were pipetted out in vials and the activity was measured in a well-type sodium iodide-thallium scintillation crystal assembly. In later work, the aqueous and the organic phases were made up to the mark in

standard volumetric flasks which had been previously matched with respect to a NaI (Tl) crystal—fixed geometry set-up (20 ml. of a high counting Co^{60} aqueous solution taken in each flask and made up to the mark with water gave counts which agreed to within about 0.2%). The percentage retentions were calculated from the above measurements.

In a few tests, cobalt sulphate solution alone was used to extract the cobaltous activity from the benzene solution of the irradiated sample. It was observed that, although the benzene solution had to be struck a larger number of times, the final value of the retention was identical with that obtained by using the EDTA mixture for extraction. This indicated that the EDTA solution extracted only those species which exchanged readily with cobaltous ions.

It may be pointed out that the species that cannot be extracted by EDTA must be in the same chemical state as that of the parent complex (or perhaps some form very closely allied to it).

When an aliquot was dissolved in benzene, allowed to evaporate to dryness and then subjected to thermal treatment, no change in the value of retention occurred, showing that the metastable specie is destroyed by dissolution in a solvent.

DATA AND OBSERVATIONS

Single stage annealing.—Isothermal runs were made at 50°, 71°, 82.5°, 92°, 101.5°, 111°, 116.5° and 122.5° C. and the data is given in the following tables. It will be observed that the initial value of retention in Tables I–IV (*viz.*, 21.1%) is different from that in Tables V–VIII (*viz.*, 20.4%) due to the annealing which occurred during storage at room temperature.

Retention (R) *vs.* time (t) in hours has been plotted for Tables III–VIII in Fig. 1. It would be seen that, at each temperature R reaches a saturation value (R_∞) characteristic of the temperature of the isothermal run, after which even prolonged heating produces no change. The values of ($R_\infty - R$) are given in the last column of the tables and are plotted against ' t ' on the semi-log paper in Figs. 2 and 3. The plots are found to be perfectly linear, indicating that annealing is governed by first order kinetics. The time of half-reaction ($t_{\frac{1}{2}}$) has been determined from the semi-log plot for each temperature and its value and that of ' k ', the specific reaction rate are recorded at the foot of each table.

Multistage annealing.—In order to study the effect of previous thermal treatment on annealing behaviour the following multistage heating experiments were undertaken.

TABLE I

Temperature 50 ± 1° C.

Time of heating days	Percentage Retention	($R_{\infty} - R$)
0	21.1	5.7
1	22.7	4.1
2	23.6	3.2
3	24.7	2.1
6	25.85	0.95
10	26.2	0.6
14	26.5	0.3
21	26.8	
28	{ 26.7 26.9	

R_{∞} : 26.8%; $t_{\frac{1}{2}}$: 55 h./00 m.; 'k': $0.35 \times 10^{-5} \text{ sec.}^{-1}$

TABLE II

Temperature 71 ± 0.2° C.

Time of heating	Percentage Retention	($R_{\infty} - R$)
Hrs. Min.		
0—00	21.1	8.5
4—00	22.8	6.8
8—00	24.1	5.5
18—00	26.1	3.5
30—00	27.6	2.0
40—00	28.5	1.1
57—00	29.2	0.4
72—00	29.4	0.2
96—00	29.6	
120—00	29.5	
144—00	29.6	
168—00	29.7	

R_{∞} : 29.6%; $t_{\frac{1}{2}}$: 13h./15 m.; 'k': $1.45 \times 10^{-5} \text{ sec.}^{-1}$

TABLE III
Temperature $82.5 \pm 0.5^\circ \text{C}$.

Time of heating		Percentage Retention	$(R_\infty - R)$
Hrs.	Min.		
0	00	21.1	9.9
2	00	22.4	8.6
4	00	23.4	7.6
8	00	25.0	6.0
18	00	27.7	3.3
32	00	29.5	1.5
56	00	30.6	0.4
72	00	30.9	
87	00	31.0	
100	00	30.9	

R_∞ : 31.0%; $t_{1/2}$: 11 h./37 m.; ' k ': $1.64 \times 10^{-5} \text{ sec.}^{-1}$

TABLE IV
Temperature $92.0 \pm 0.2^\circ \text{C}$.

Time of heating		Percentage Retention	$(R_\infty - R)$
Hrs.	Min.		
0	00	21.1	16.9
4	00	25.0	13.0
8	00	28.6	9.4
15	00	32.6	5.5
20	00	34.0	4.0
24	00	35.0	3.0
28	00	35.6	2.4
32	00	36.5	1.5
42	12	37.1	0.9
55	00	37.5	0.5
71	00	38.0	
87	00	38.1	
96	00	38.0	

R_∞ : 38.0%; $t_{1/2}$: 9 h./48 m.; ' k ': $1.96 \times 10^{-5} \text{ sec.}^{-1}$

TABLE V

Temperature $101.5 \pm 0.5^\circ \text{C}$.

Time of heating	Percentage Retention	($R_\infty - R$)
Hrs. Min.		
0—00	20.4	32.2
1—30	24.7	27.9
3—00	28.3	24.3
5—30	33.3	19.3
9—30	38.2	14.4
14—00	43.8	8.8
15—00	44.5	8.1
16—00	45.2	7.4
17—00	45.8	6.8
21—00	48.0	4.6
26—00	50.0	2.6
34—00	51.1	1.5
55—00	52.3	
69—00	52.9	
72—00	52.5*	

 R_∞ : 52.6%; $t_{\frac{1}{2}}$: 7 h./36 m.; 'k': $2.53 \times 10^{-5} \text{ sec.}^{-1}$

* Recent check value on the oil-bath.

TABLE VI

Temperature $111.0 \pm 0.5^\circ \text{C}$.

Time of heating	Percentage Retention	($R_\infty - R$)
Hrs. Min.		
0—00	20.4	35.4
1—00	25.8	30.0
2—00	28.3	27.5
3—00	31.1	24.7
5—00	36.9	18.9
7—00	40.4	15.4
9—00	43.8	12.0
11—00	45.5	10.3
15—36	50.5	5.3
22—30	53.0	2.8
33—00	55.1	0.7
57—00	55.9	
70—00	55.7	

 R_∞ : 55.8%; $t_{\frac{1}{2}}$: 5 h./42 m.; 'k': $3.77 \times 10^{-5} \text{ sec.}^{-1}$

TABLE VII
Temperature $116.5 \pm 0.5^\circ \text{C}$.

Time of heating	Percentage Retention	$(R_\infty - R)$
Hrs. Min.		
0—00	20.4	39.7
1—30	30.5	29.6
3—00	35.9	24.2
5—00	41.8	18.3
6—00	45.3	14.8
7—00	48.4	11.7
8—00	49.2	10.9
9—00	51.4	8.7
10—00	52.2	7.9
11—00	53.8	6.3
12—00	54.9	5.2
18—00	57.8	2.3
21—00	59.3	0.8
42—00	59.8	
56—00	60.5	
65—10	59.6	
80—00	60.3	

R_∞ : 60.1%; $t_{\frac{1}{2}}$: 4 h./12 m.; ' k ': $4.58 \times 10^{-5} \text{ sec.}^{-1}$

TABLE VIII
Temperature $122.5 \pm 0.5^\circ \text{C}$.

Time of heating	Percentage Retention	$(R_\infty - R)$
Hrs. Min.		
0—00	20.4	45.7
0—30	25.0	41.1
1—30	34.8	31.3
3—00	46.3	19.9
4—00	50.9	15.2
5—00	54.2	11.9
6—00	58.4	7.7
7—00	59.0	7.1
16—00	65.3	0.8
24—00	66.0	
54—00	66.2	

R_∞ : 66.1%; $t_{\frac{1}{2}}$: 2h./36 m.; ' k ': $7.40 \times 10^{-5} \text{ sec.}^{-1}$

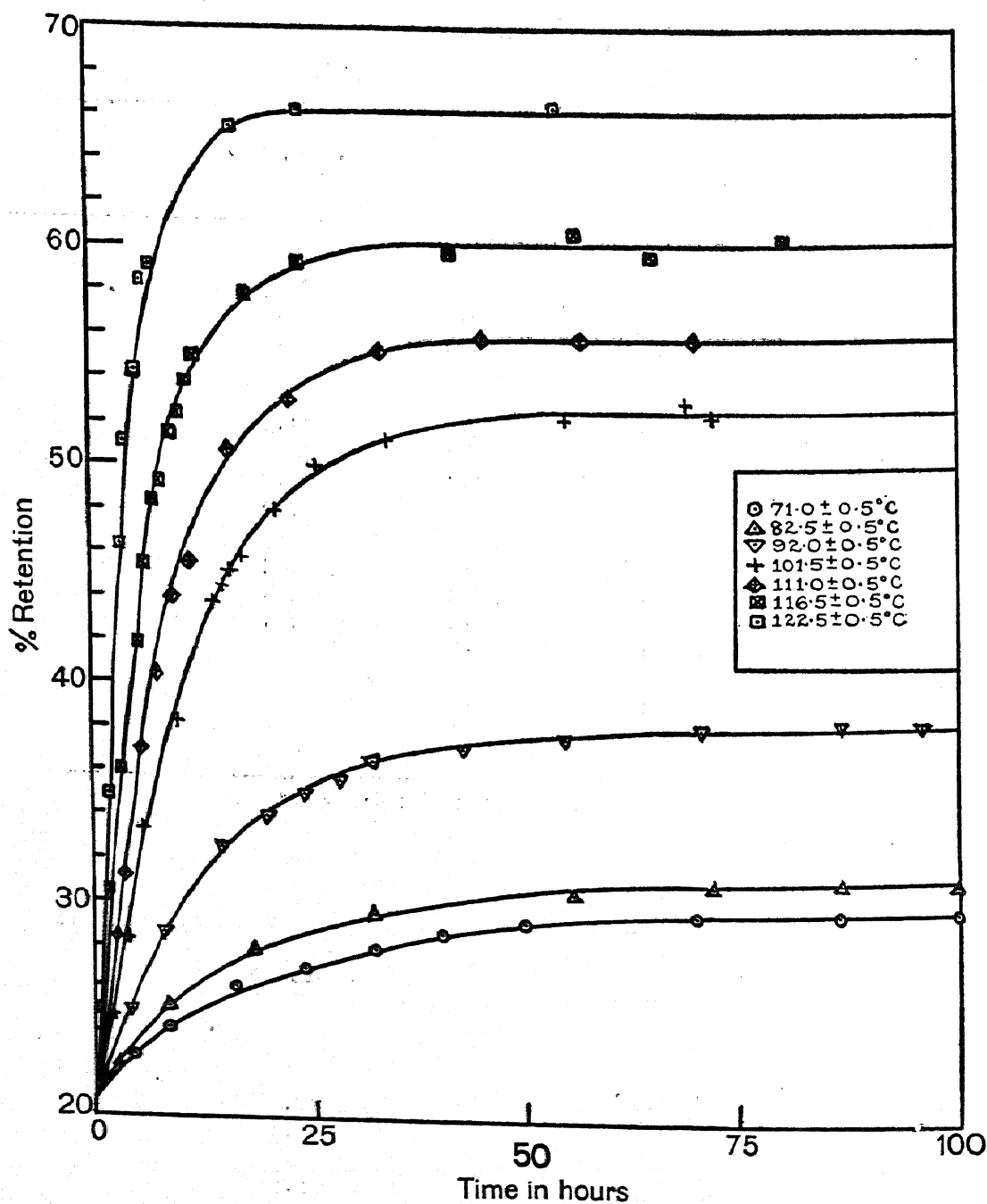


FIG. 1

An adequate portion from the irradiated bulk sample was heated at 82.5°C. for a period longer than that required to attain R_{∞} . Small aliquots were drawn from this heated sample and these along with the remainder were reheated at 92°C. The former were withdrawn at different periods to work out the kinetics, while the latter was heated to attain R_{∞} . The process was repeated through 101.5°, 116.5°, and 122.5° C.

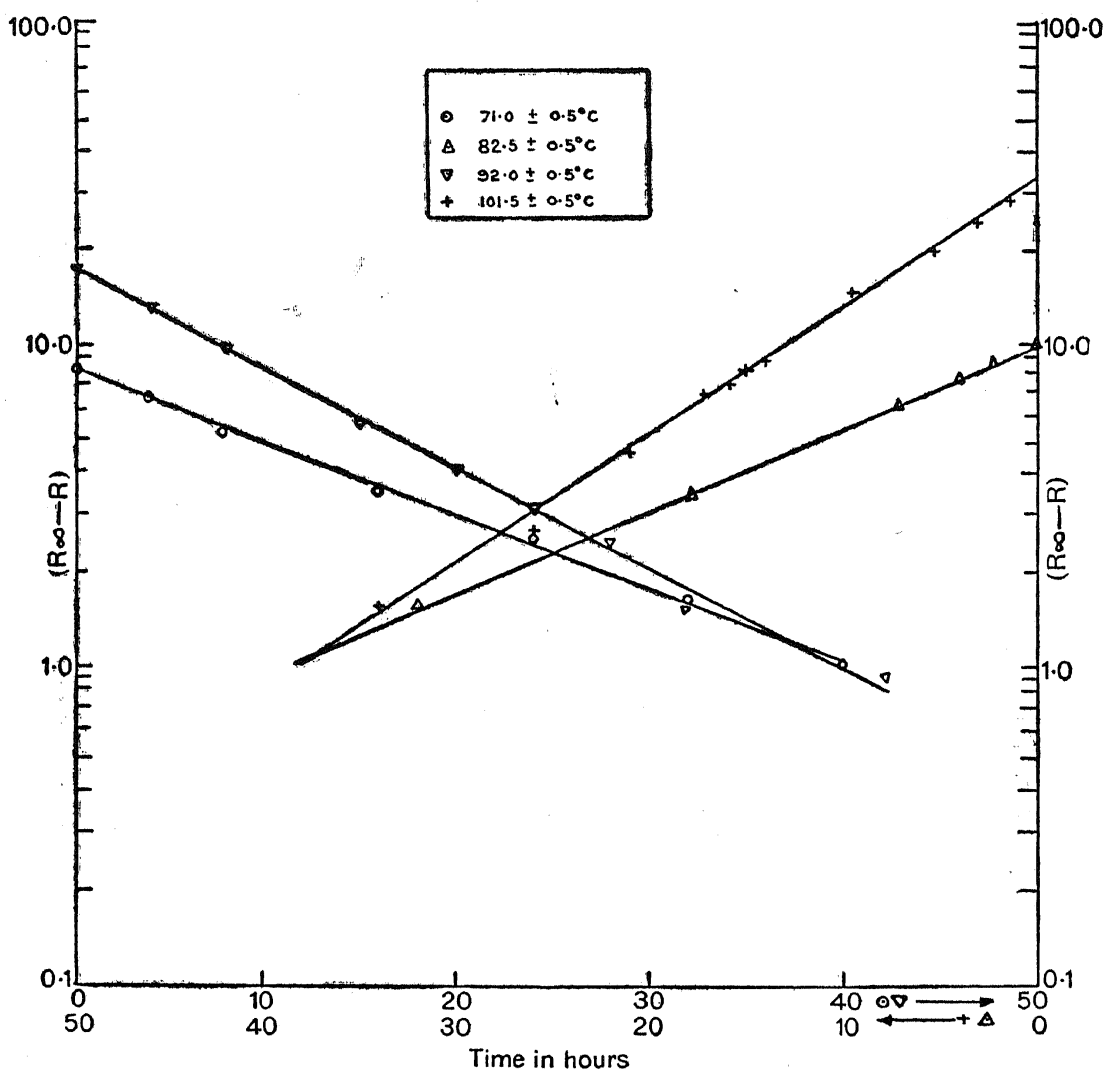


FIG. 2

Thus, the samples used for the run at 122.5° had previously been subjected to isothermal annealing to saturation values of retention successively at 82.5° , 92° , 101.5° and 116.5° . The data is given in Tables IX–XII and plotted in Fig. 4. The R_∞ values for multistage heating tests are summarized in Table XIII, in which, for the sake of comparison, R_∞ values for single stage annealing at the corresponding temperatures are also shown along with.

Value of R_∞ for multistage heating is lower than that for the single stage for the corresponding temperature. The rate constants also exhibit a marked decrease as compared to those for single stage annealing.

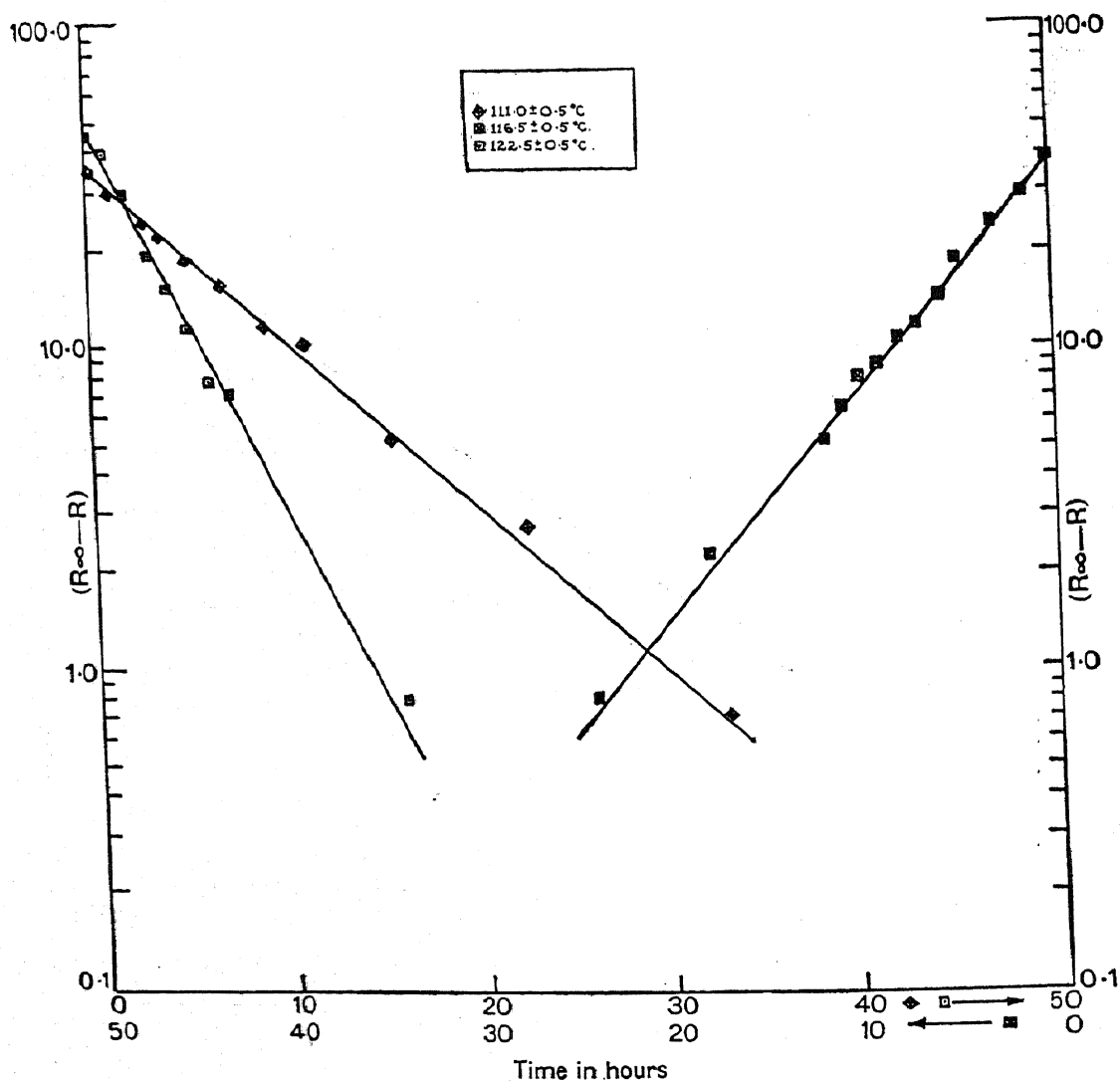


FIG. 3

Two stage-combination heating.—To gain further insight into the effect produced by the history of the heat treatment, the undermentioned investigations were carried out.

In one set, the initial treatment consisted of one step thermal annealing to R_∞ at a given temperature, and the final annealing at various higher temperatures. In Table XIV, the first column gives the temperature at which the final annealing was done, the second column the values of R_∞ at the corresponding temperature, with no previous heat treatment, columns 3–6 give the values of R_∞ obtained at temperature mentioned at the head of each column. The values of R_∞ for multistage annealing are given in the last column for the sake of comparison.

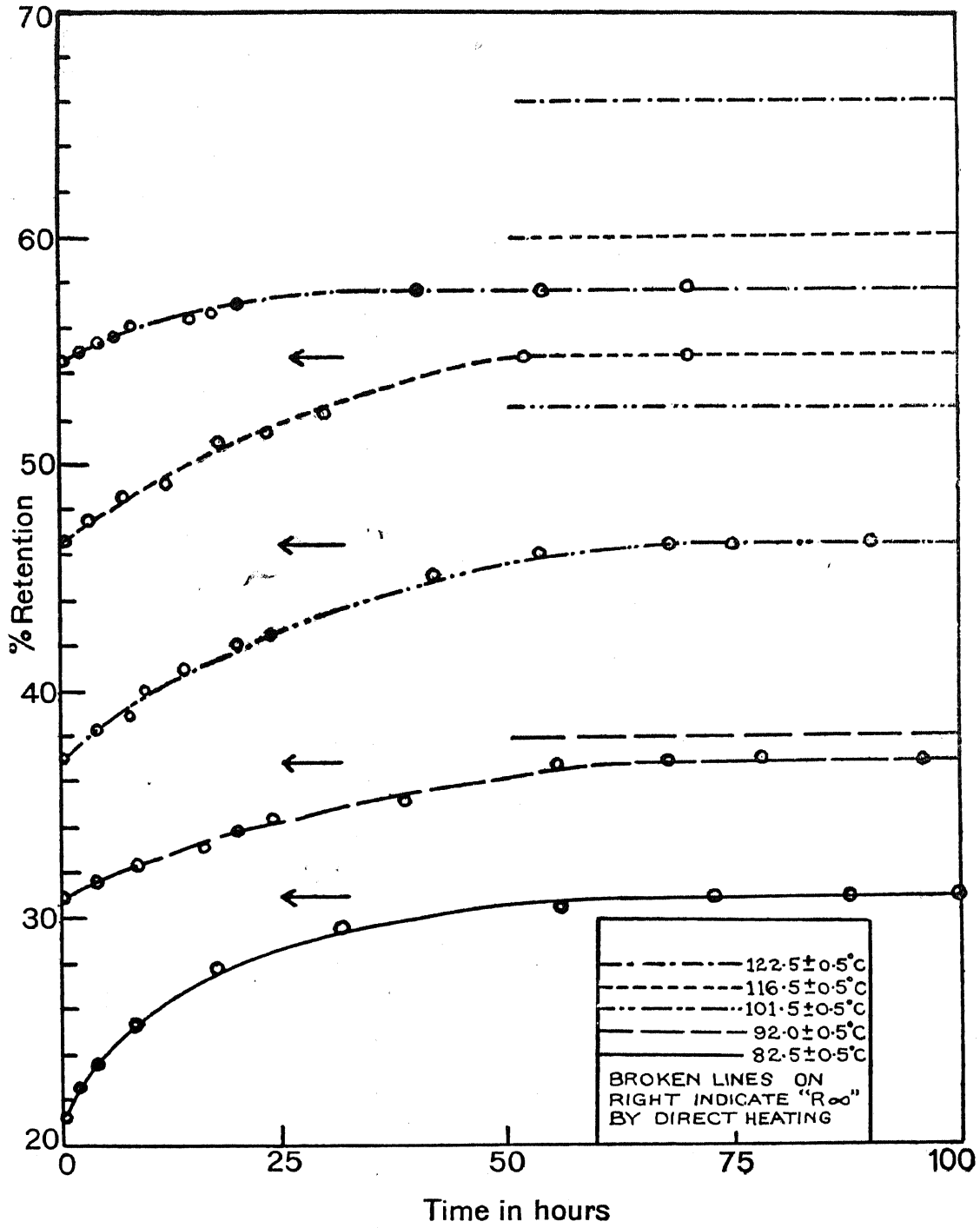


FIG. 4

TABLE IX

*Multistage annealing*Run at $92.0 \pm 0.2^\circ \text{C}$.Thermal history: 80 hrs. at 82.5°C .

Time of heating		Percentage Retention 'R'
Hrs.	Min.	
0	00	31.0
4	00	31.6
8	00	32.3
16	00	33.2
20	00	33.8
24	00	34.3
39	00	35.3
56	00	36.7
68	00	36.9
78	00	37.1
96	00	37.0

$$R_{\infty} : 37.0\%; t_{\frac{1}{2}} : 22 \text{ h./31 m.}; 'k' : 0.85 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE X

*Multistage annealing*Run at $101.5 \pm 0.2^\circ \text{C}$.Thermal history: 80 hrs. at 82.5°C . and then 78 hrs. at 92°C .

Time of heating		Percentage Retention 'R'
Hrs.	Min.	
0	00	37.0
4	00	38.2
8	00	39.2
10	00	40.0
14	00	41.0
20	00	42.0
24	00	42.5
42	00	45.0
54	00	46.0
68	00	46.5
74	00	46.5
90	00	46.6

$$R_{\infty} : 46.5\%; t_{\frac{1}{2}} : 19 \text{ h./00 m.}; 'k' = 1.01 \times 10^{-5} \text{ sec.}^{-1}$$

TABLE XI

*Multistage annealing*Run at $116.5 \pm 0.2^\circ \text{C}$.Thermal history: 80 hrs. at 82.5°C .,
78 hrs. at 92°C . and then
68 hrs. at 101.5°C .

Time of heating		Percentage Retention 'R'
Hrs.	Min.	
0	00	46.5
2	00	47.5
5	00	48.1
9	00	48.7
15	00	50.4
20	00	51.0
24	00	51.6
30	00	52.6
52	00	54.8
70	00	54.9

 R_∞ : 54.9%; $t_{1/2}$: 17 h./30 m.; ' k ': $1.10 \times 10^{-5} \text{ sec.}^{-1}$

TABLE XII

*Multistage annealing*Run at $122.5 \pm 0.2^\circ \text{C}$ Thermal history: 80 hrs. at 82.5°C .,
78 hours at 92°C .
68 hours at 101.5°C . and then
56 hours at 116.5°C .

Time of heating		Percentage Retention 'R'
Hrs.	Min.	
0	00	54.9
2	00	55.1
4	00	55.5
6	00	55.7
8	00	56.0
15	00	56.5
17	00	56.7
20	00	57.0
40	00	57.8
54	00	57.9
70	00	58.0

 R_∞ : 57.9%; $t_{1/2}$: 13 h./02 m.; ' k ': $1.48 \times 10^{-5} \text{ sec.}^{-1}$

TABLE XIII

Summary of results of multistage heating tests

Temp. ° C.	R_{∞}		Rate constant (k) $\times 10^{-5}$ sec. $^{-1}$	
	Single stage	Multistage	Single stage	Multistage
82.5	31.0%	..	1.64	..
92.0	38.0%	37.0%	1.96	0.85
101.5	52.6%	46.5%	2.53	1.01
116.5	60.1%	54.9%	4.58	1.10
122.5	66.1%	57.9%	7.40	1.48

TABLE XIV

 R_{∞} is obtained by combination of two-stage heating experiments

Final heating temp. ° C.	Previous treatment					Value of multistage experiments
	None	82.5° C.	92.0° C.	101.5° C.	116.5° C.	
92.0	38.0*	37.0
101.5	52.5*	50.2	49.2	46.5
116.5	60.2*	58.8	57.7	56.0	..	54.9
122.5	66.2*	64.1	62.9	62.0	61.1	57.9

* R_{∞} values redetermined for this set.

An essential feature of the above data for the temperatures studied, is that the higher the temperature of the initial thermal treatment,† the greater is the drop in the values of R_{∞} , as compared to its value for a single stage annealing at the higher temperature.

† With the reservation that if the difference between the temperature of the initial and final anneal is less than a certain value, the 'retention' would suffer only a slight or no change on undergoing the final treatment, e.g., when the samples are heated via 118.6° C. and 120.5° C. to 122.5° C. the values of R_{∞} 62.0% and 63.9% undergo no change. Similarly when heated via 99.5° C. to 101.5° C. the value of R_{∞} remains practically constant (49.1%) while when heated via 97.5° C., R_{∞} increases from 45% to 46% at 101.5° C. Thus within this narrow temperature range the difference in the value of R_{∞} in the two stage and single stage heating may be very small.

In the second set of two-stage annealing tests, experiments were done, in the first stage of which samples were heated at different temperatures, for various periods, so as to attain nearly identical values of retention. They were then annealed to saturation values at (a) 101.5° C., and (b) 122.5° C. The results are presented in Table XV.

TABLE XV

Initial treatment			Final treatment			
Temp. ± 0.2° C.	Time of heating	Percentage retention	A: at 101.5 ± 0.2° C.		B: at 122.5 ± 0.2° C.	
			Time of heating	Percentage retention	Time of heating	Percentage retention
	Hrs. Min.		Hrs. Min.		Hrs. Min.	
101.5	15 - 48	45.1	72 - 00	52.4	30 - 00	64.65
111.0	9 - 54	45.0	72 - 00	51.3	30 - 00	64.3
116.5	5 - 48	45.2	72 - 00	51.0	30 - 00	64.0
122.5	2 - 54	45.2	72 - 00	50.8	30 - 00	66.0

The results indicate that the previous thermal history is reflected in the values of R_{∞} for the final annealing, in spite of the fact that they had the same retention values at the end of the preliminary treatment.

In another set, aliquots were heated for varying periods of time at 116.5° C., and reheated to saturation anneal at a lower temperature, *viz.*, 101.5° C. The general trend of the change in retention is the same as observed in the other experiments in this series as shown in Table XVI.

It will be observed that as a result of heating at the higher temperature, when the retention acquires a value equal to or greater than R_{∞} for the lower temperature (101.5° C.), it is not affected by the final thermal treatment. For example the value of R for 11 hours heating at 116.5° is 53.8 (Table XVI) and the same value has been obtained even after further heat treatment for 72 hours at the lower temperature 101.5° C.

DISCUSSION

The fact that the plot of $\log (R_{\infty} - R)$ [*viz.*, log of the concentration of the metastable specie destined to anneal at a given temperature] *versus* time, gives a distinctly linear plot for isothermal annealing at each temperature studied, and also that, once R_{∞} is attained, further heating at

TABLE XVI

Time of heating at $116.5 \pm 0.2^\circ \text{C}$.	Saturation values obtained at $101.5 \pm 0.2^\circ \text{C}$. after 72 hours heating
0—20	51.9 } 52.1 } 52.0
0—40	51.65 } 51.54 } 51.6
1—00	51.2 } 51.2 } 51.2
7—00	50.4 } 50.6 } 50.5
9—54	52.5 } 52.5 } 52.5
11—00	53.7 } 53.9 } 53.8

that temperature does not affect the value of retention, go to show that the increase in R_∞ with temperature can hardly be accounted for by the existence of a wide 'spectra of activation energies' associated with the annealing of a variety of damage centres (*cf.* radiation damage in metal, graphite,^{9, 10} etc.). The observation that heating at a higher temperature, after isothermal annealing at a lower temperature to infinity values (R_∞), results in further annealing eliminates the possibility of the existence of 'conventional' competing reactions,[‡] which could have ordinarily accounted for the temperature dependence of R_∞ . Hence, it appears that higher concentrations of the metastable specie undergoing annealing are made available with the increase of temperature by a 'thermally activated' intermediate process.

It was felt that it would be interesting to study the effect, if any, of prolonged heating at a lower temperature on the metastable specie destined to anneal at a higher temperature. Aliquots were, therefore, heated for varying periods of time after attainment of saturation anneal at 101.5°C .

[‡] where once the reaction is completed, the fate of the reacting specie, at any temperature, is irreversibly determined by the juxtaposition of more than one reaction, and no further change is produced by changing the temperature.

n reheated to maximum anneal at 122.5° C. The data are given in KVII. The decrease in the value of R_{∞} (last column) is of a very magnitude and is suggestive of very slight, if any, degradation or some process incapacitating later thermal annealing of the specie. Also, of the above observations, the possibility of the existence of some a dynamic equilibrium after the saturation anneal is achieved at ten temperature, is discounted.

TABLE XVII

Preliminary heating at 101.5° C. for various periods beyond attainment of R_{∞} before annealing to infinity at 122.5° C.

Initial treatment at $101.5 \pm 0.2^{\circ}$ C. Final treatment at $122.5 \pm 0.2^{\circ}$ C.

Time of heating	Percentage Retention (R_{∞})	Time of heating	Percentage Retention (R_{∞})
5—00	(a) 52.6 } (b) 52.8 } (52.7)	30—00	62.0
3—00	(a) 52.7 } (b) 52.8 } (52.75)	”	(a) 61.8 } (b) 61.9 } (61.85)
3—00	(a) 52.5 } (b) 52.6 } (52.55)	”	(a) 61.5 } (b) 61.7 } (61.6)
4—00	(a) 52.5 } (b) 52.6 } (52.55)	”	61.5

The plot of $\log 'k'$ versus $1/T$ (Fig. 5) shows a marked curvature, ordinarily could have been roughly accounted for by the existence of more annealing processes predominating at different temperatures, and each with different values of activation energies. Since the plot of $-\log R$ versus t is strictly linear at all the temperatures studied, among the ones where the $\log k$ versus $1/T$ plot shows a large variation in slope, it may be concluded that there is only a single annealing process exhibiting an apparent wide variation in activation energy and pre-exponential factor, as shown in Table XVIII. This indicates that the annealing process is not a simple unimolecular reaction but is rather complex, perhaps involving several steps.

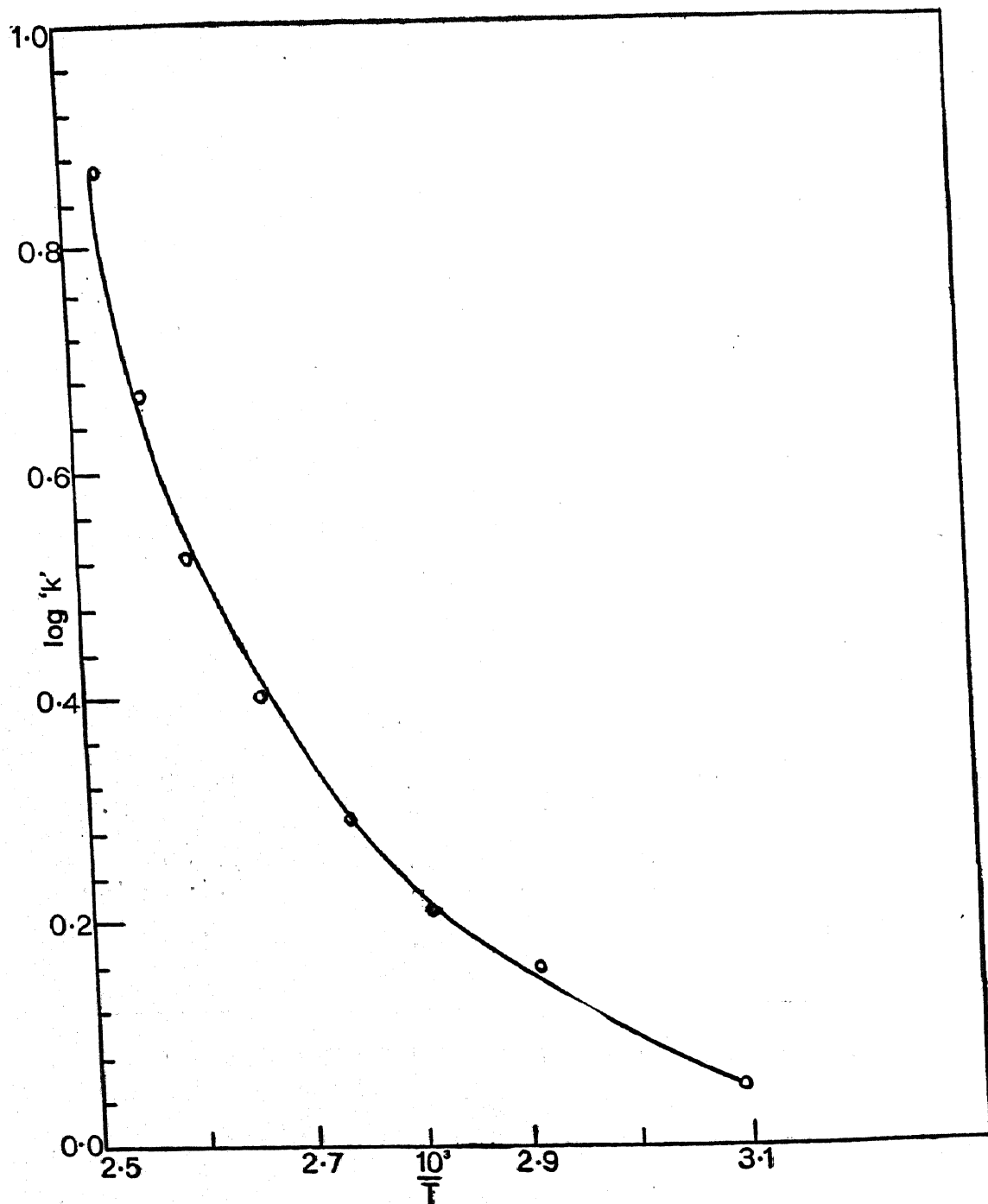


FIG. 5

The rate constant, ' k ' and the saturation value of retention, R_∞ for any isothermal run are a function of the previous thermal history, as shown in the earlier sections. This can be explained by assuming the existence of competing reactions which, as has been stated, appear to be rather complex and involve more than one step in a fashion that they (reactions) mutually

influence each other. If the latter was not true, the value of 'k' would not have been affected by previous thermal treatment.

TABLE XVIII
Activation energies interpolated from Fig. (log k vs. 1/T)

Temperature °C.	Activation energy E	Frequency factor A (calculated from $\ln k = \ln A - E/RT$)
50.0	2.12	..
82.5	3.06	$10^{-5.91}$
92.0	5.66	$10^{-4.81}$
101.5	8.03	$10^{-1.96}$
111.0	11.95	$10^{-0.13}$
116.5	18.54	10^4
122.5	35.25	$10^{13.4}$

Perhaps, it can be visualized that during an isothermal run the fate of the metastable specie is decided by two or more competing paths available for 'stabilization'. One of the processes is that of irreversible annealing to form the parent cobaltic specie (or some other specie closely allied to the parent which, however, does not appear probable). The other main process seems to consist of 'setting' or 'trapping'[‡] of the metastable specie with well-defined but variable depths—a physical process which inhibits, at the particular temperature, the annealing of the metastable specie directly or indirectly through an intermediate mechanism. But thermal activation at a higher temperature can result in a fraction of the metastable specie becoming available, directly or indirectly, for annealing. A third possible course can be the participation of the metastable specie in a process leading to irreversible degradation to the cobaltous state.

In the search for some tangible evidence for the above idea of competitive reactions, the following experiment was planned. If samples are heated for increasing periods of time at a fixed temperature and subsequently reheated to saturation value at a higher temperature, the trend followed by the decrease

[‡] This concept has been used by Lomer and Cottrell (*Phil. Mag.*, 1955, 46, 711) in a different context and in a restricted sense. Here it is intended to have a wider significance.

ation, R_{∞} for an
atory, as shown in
the existence of
the rather complex
reactions) mutual

in retention with longer periods of preliminary heating, could reflect the existence of competing reactions, as well as their numbers. Two sets of experiments were performed for 101.5°C. to 116.5°C. , and 116.5°C. to 122.5°C. The data are given in Tables XIX and XX.

TABLE XIX

Time of heating at $101.5 \pm 0.2^{\circ}\text{C.}$		Saturation values obtained at $116.5 \pm 0.2^{\circ}\text{C.}$ after 72 hrs. of heating	$(R_t' - R_{\infty}')$
Hrs.	Min.		
0	00	60.1 (R_t' for $t = 0$)	4.0
0	30	59.0 } 59.2 } 59.1	3.0
1	00	58.8 } 58.6 } 58.7	2.6
1	30	58.35 } 58.46 } 58.4	2.3
2	30	58.1 } 57.9 } 58.0	1.9
4	00	57.6 } 57.6 } 57.6	1.5
6	00	57.35 } 57.44 } 57.4	1.3
8	00	57.1 } 57.3 } 57.2	1.1
10	00	56.9 } 57.1 } 57.0	0.9
16	00	56.5 } 56.7 } 56.6	0.5
21	00	56.4 56.4	0.3
26	00	56.2 } 56.2 } 56.2	0.1
72	00	56.0 } 56.2 } 56.1	

TABLE XX

Time of heating at $116.5 \pm 0.2^\circ \text{C.}$	Saturation values obtained at $122.5 \pm 0.2^\circ \text{C.}$ after 45 hrs. of heating	$(R_t' - R_\infty')$
Hrs. Min.		
0—00	66.1 (R_t' for $t = 0$)	4.9
0—24	64.5 } 64.4 } 64.45	3.25
0—48	63.0 } 63.3 } 63.15	1.95
1—12	62.75 } 62.85 } 62.8	1.6
1—30	62.65 } 62.5 } 62.57	1.37
2—00	62.4 } 62.2 } 62.3	1.1
2—30	62.2 } 62.1 } 62.15	0.95
3—00	62.1 } 61.9 } 62.0	0.8
10—00	61.8 } 61.7 } 61.75	0.55
22—00	61.5 61.5	0.3
45—00	61.2 } 61.2 } 61.2	

The values for $R_t' - R_\infty'$ for the two sets (where R_t' is the value obtained from an aliquot heated for period 't' at the lower temperature, and reheated to saturation value at the selected higher temperature and R' is the value attained by an aliquot after preliminary heating to saturation anneal at the lower temperature and reheated to saturation value at the higher temperature) are plotted in Fig. 6. On analysis, the curves yield two linear plots indicating the existence of two first-order competitive reactions responsible for either removing the metastable specie from the site of the reaction or incapacitating

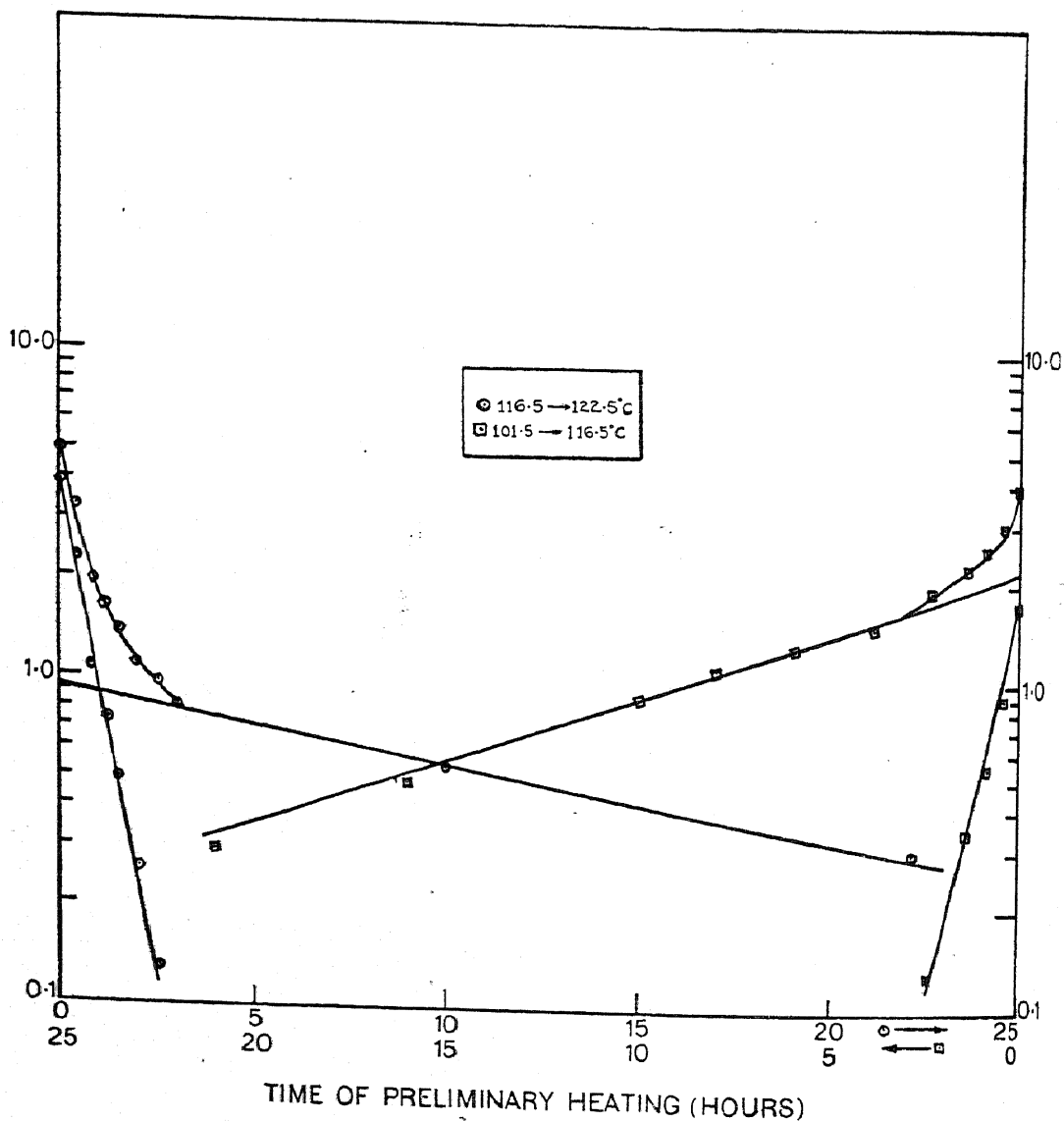


FIG. 6

it from annealing. In short, there are perhaps three competing processes operating, if only one is assumed for the annealing. As regards the nature of the damage centre undergoing annealing, some preliminary considerations come to the forefront. Can the thermal annealing be accounted for, by radical reactions in the 'brush-heap' of randomly fragmented molecules (as postulated by Willard and co-workers¹¹ for organics)? It is unlikely that this mechanism could be playing any significant role here for a variety of reasons. Firstly, it is rather difficult to conceive of such 'neat reconstitution' of the cobaltic chelate, from the debris (formed by random fragmentation of molecules). Secondly, such a process would place rather stringent demands on

the stability of the radicals concerned, especially at higher temperatures. Thirdly, barring the radicals which are in immediate neighbourhood, the reaction would be diffusion-controlled and hence obeying second-order kinetics, which is contrary to the present findings. The other possibility, which sounds more plausible, is the existence of 'configurational' and 'electronic' metastable states which are amenable to thermal and also irradiation annealing. Work on irradiation annealing will be published elsewhere.

ACKNOWLEDGEMENTS

We are particularly thankful to Mr. W. S. Eastwood of the Isotope Division, A.E.R.E., Harwell, for taking pains in arranging irradiation in BEPO under specified conditions. We express our appreciation of the assistance of Mr. S. Ramaswamy in the maintenance of the electronic equipment. Our gratitude is due to Prof. B. Peters and Dr. K. S. Singwi for the stimulating discussion.

SUMMARY

Isothermal annealing has been found to follow first-order kinetics for the range of temperature studied. It has been found that the previous thermal history is reflected in the rate-constant (k) and the plot of $\log k$ versus $1/T$ exhibits a marked curvature. This has been explained as due to the fact that the annealing reaction leading to the parent specie is not a simple unimolecular one but is complex, involving several stages which in turn exercise mutual influence on other competing reactions preventing annealing.

During an isothermal anneal, the fate of the metastable specie is decided by three competitive reactions—one for annealing to the parent specie and the other two working in the reverse direction—the existence of which have been shown by graphical analysis of experimental data. One of the latter processes seem to be amenable to reversal in the sense that more metastable specie becomes available for anneal at a higher temperature after a run to infinity at a lower one. It seems that this process consists of 'setting' or 'trapping' of the metastable specie with variable depths—a physical process which inhibits at the particular temperature, the annealing of the metastable specie.

Considerable experimental work would be required to elucidate unambiguously the nature of the damage centre but the indications are that it is of a 'configurational' or 'electronic' nature, as it is amenable to both 'thermal' as well as 'radiation' annealing.

REFERENCES

1. Green, J. H. and Maddock, *Nature*, 1949, **164**, 788.
A. G.

2. Rieder, W., Broda, E. and Erber, J. *Monatsh*, 1950, **81**, 657.
3. Cobble, J. W. and Boyd, G. E. *J. Am. Chem. Soc.*, 1952, **74**, 1282.
4. Green, J. H., Harbottle and Maddock, A. G. *Trans. Farad. Soc.*, 1953, **49**, 1413.
5. Maddock, A. G. and De Maine, M. M. *Can. J. Chem.*, 1956, **34**, 275.
6. Aten, A. H. W. and Van Berkum, J. B. M. *J. Am. Chem. Soc.*, 1950, **72**, 3273.
7. Zuber, A. V. .. NYO-6142 BNL, Columbia University, 1954.
8. Gach, F. .. *Monatsh*, 1900, **21**, 105.
9. Glen, J. W. .. *Adv. Phys.*, 1955, **4**, 403.
10. Burton, M. and Neubert, T. J. *J. Ap. Phys.*, 1956, **27**, 557.
11. Willard, J. W. .. *Ann. Rev. Nu. Sci.*, 1953, **3**, 193.
12. West, B. .. *J. Chem. Soc.*, 1952, 3115.
13. Herr, Wilfrid .. *Z. Elektrochemie*, 1952, **56**, 911.