

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 The Spin-lattice Relaxation Time $T_1$

The values for spin-lattice relaxation time,  $T_1$ , were measured as a function of the temperature. The experimental results for measuring  $T_1$  are shown in Table I. The maximum experimental uncertainty in the determination of  $T_1$  was estimated to be  $\pm 10\%$ , due to uncertainty in distinguishing null signal exactly and in setting the initiating  $180^\circ$  pulse. The plots of  $\log(T_1^{-1})$  against  $10^3/T$ , and  $\log(T_1)$  against  $10^3/T$ , where  $T$  is the absolute temperature in degrees Kelvin are shown in Fig.4.1 and Fig.4.2 respectively. Both curves show our experimental  $T_1$  variation with temperature.  $T_1$  is longer at higher temperature. Measurements of  $T_1$  for the same sample had been repeated many times. The results of these measurements (Table I) agree within 5 per cent.

From the basic theory given in chapter II, the results of the derivation of spin-lattice relaxation time are summarized in equations (2.11) and (2.14) which can now be expressed as :

$$\left(\frac{1}{T_1}\right)_{\text{rot}} = 2\pi \gamma^4 \hbar^2 a^3 \eta / b^6 k T,$$

$$\left(\frac{1}{T_1}\right)_{\text{transl}} = \frac{3}{2} \pi^2 \gamma^4 \hbar^2 N_0 \eta / k T.$$

Substituting the known numerical values<sup>13</sup>  $a = 1.38 \times 10^{-8}$  cm.,  $T = 303^\circ\text{K}$ ,  $b = 1.51 \times 10^{-8}$  cm., and  $\eta = 0.798 \times 10^{-2}$  poise,  $\gamma = 2.68 \times 10^4$  gauss<sup>-1</sup> sec<sup>-1</sup> and  $N_0 = 7 \times 10^{22}$  cm.<sup>-3</sup>, in the two equations above we find

$$(T_1)_{\text{rot}} = 6.7 \text{ sec. and } (T_1)_{\text{transl}} = 10.7 \text{ sec.}$$

The resultant spin-lattice relaxation time,  $T_1$ , is determined from the relation

$$\left(\frac{1}{T_1}\right) = \left(\frac{1}{T_1}\right)_{\text{rot}} + \left(\frac{1}{T_1}\right)_{\text{transl}}$$

We find  $T_1 = 4.1$  sec. for temperature  $303^\circ\text{K}$  or  $30^\circ\text{C}$ .

At  $100^\circ\text{C}$ ,  $\eta = 0.283 \times 10^{-2}$  poise, we find

$$(T_1)_{\text{rot}} = 22.2 \text{ sec.}, (T_1)_{\text{transl}} = 33.8 \text{ sec.}, T_1 = 13.5 \text{ sec.}$$

Our measured value of  $T_1$  are 3.5 sec. and 7.2 sec. at  $30^\circ\text{C}$  and  $100^\circ\text{C}$  respectively.

In Fig. 4.2 the results of  $T_1$  measurement by Krynicki<sup>13</sup>, and by Simpson and Carr<sup>4</sup> are also compared with those obtained here. At temperatures below  $30^\circ\text{C}$  our result of  $T_1$  can be considered to be in agreement with both results, but at high temperatures it deviates from them. At  $30^\circ\text{C}$ , the value from this work is 13 % lower than that of Krynicki, 8 % lower than that of Simpson and Carr, and 12 % lower than that of the theory. At  $100^\circ\text{C}$ , it is 43 % lower than that of Krynicki, 39 % lower than that of Simpson and Carr, and 45 % lower than that of the theory.

#### 4.2 Interpretation of $T_1$ Measurement and Discussion

The two contributions to  $\frac{1}{T_1}$  in water, resulting respectively from the rotational and translational motions of the water molecules and given respectively by (2.11) and (2.14), can be added together and rewritten as

$$\frac{1}{T_1} = \left( \frac{a^2}{b^2} \right) \left( \frac{\gamma^4 \hbar^2}{3Db^4} \right) \left[ 1 + \frac{3\pi}{4} \frac{b^6 N_0}{a^3} \right] \dots\dots(4.1)$$

where  $a$  is the radius of the hard sphere to which the molecules is approximated in the Stokes-Einstein formula,  $b$  is the distance between protons,  $D$  the self-diffusion coefficient of water, and  $N_0$  the number of protons  $\text{cm}^{-3}$ . Then we can write.

$$T_1 \propto D \dots\dots(4.2)$$

Studies of the temperature dependence of the self-diffusion coefficient show that  $D$  can be described by Arrhenius behaviour<sup>1</sup>

$$D = A \exp \left[ -W/(kT) \right] \dots\dots\dots(4.3)$$

where  $A$  and  $W$  are constants,  $W$  is called activation energy.

From (4.2) we have

$$T_1 = A' \exp \left[ -W / (kT) \right] \dots\dots (4.4)$$

where  $A'$  is the multiplying constant. Taking logarithm on both sides we obtain

$$\log T_1 = \log A' - W / (kT) \dots\dots\dots(4.5)$$

From (4.5), the plot of  $T_1$  against  $\frac{1}{T}$  on semi-log paper should give a straight line. In this experiment, however, the

graphs obtained are far from being straight lines. J.C. Hindman et al.<sup>14</sup> had studied the spin-lattice relaxation time in the case of  $D_2O$  and  $H_2^{17}O$ , they found that their result also deviated from being straight lines. They suggested that the temperature dependence of  $\log T_1$  could be represented as a sum of two contributions. The first process contributing to  $T_1$  arises from the breaking of hydrogen bonds, and the second process involves the rotational relaxation of single water molecules. Since the graph obtained in the present experiment curves in the same manner as  $D_2O$  result, the relaxation mechanisms involved were thought to be similar.

In spite of the difference in magnitude of  $T_1$  from various workers, all results of  $T_1$  for water (Krynicky,<sup>13</sup> Simpson and Carr<sup>4</sup> and the present result) bent down from the straight line. This shows that there must be other mechanisms contributing at high temperatures other than the translational and rotational diffusion considered in the theory in chapter II.

The fact that our result deviates from other measurements at high temperatures are at present not well understood. If we suppose that there are paramagnetic impurity present the contribution of those paramagnetic ions should only shift the whole curve down.

#### 4.3 Results and Discussion of the Relaxation Time $T_2$

The values of  $T_2$  were measured as a function of the temperature. The experimental results for measuring  $T_2$  are shown

in Table II. The experimental uncertainty in the determination of  $T_2$  was estimated to be  $\pm 20\%$ . The uncertainty was estimated from the error of the calibration of the amplitude of the spin-echo and determination of slope of the straight line. The plots of  $\log(T_2)$  against  $10^3/T$ , and  $\log(T_2^{-1})$  against  $10^3/T$  are shown in Figs. 4.3 - 4.4. The order of magnitude of  $T_2$  is only 100 msec.

Theoretically, if  $\omega\tau_c \ll 1$ ,  $T_2$  should equal to  $T_1$  (There is evidence from the experiment on dielectric relaxation that  $\tau_c$  is in the order of  $10^{-12}$  sec. and  $\omega$  at 10 Mc./sec. is of the order of  $10^8$  sec<sup>-1</sup> so  $\omega\tau_c \ll 1$ ). Our measured values of  $T_2$  are much smaller than  $T_1$ . The error might be due to the poor signal and the fact that the static field can not be held stable during the measurement. However, it had been found by Meiboom<sup>15</sup> that for water  $T_2$  could be shorter than  $T_1$  appreciably depending on pH of the sample. It is also found that<sup>16</sup> the difference between  $T_2$  and  $T_1$  results from a scalar coupling between the spin of the proton and that of <sup>17</sup>O, modulated by chemical exchange. We think that our results of  $T_2$  are not sufficiently reliable for interpretation.

Further investigation should be performed by using very pure distilled water, and to prevent the contamination by paramagnetic material from the walls of the tubes, Professor S. Ketudat suggested that the tubes should be made of Teflon.

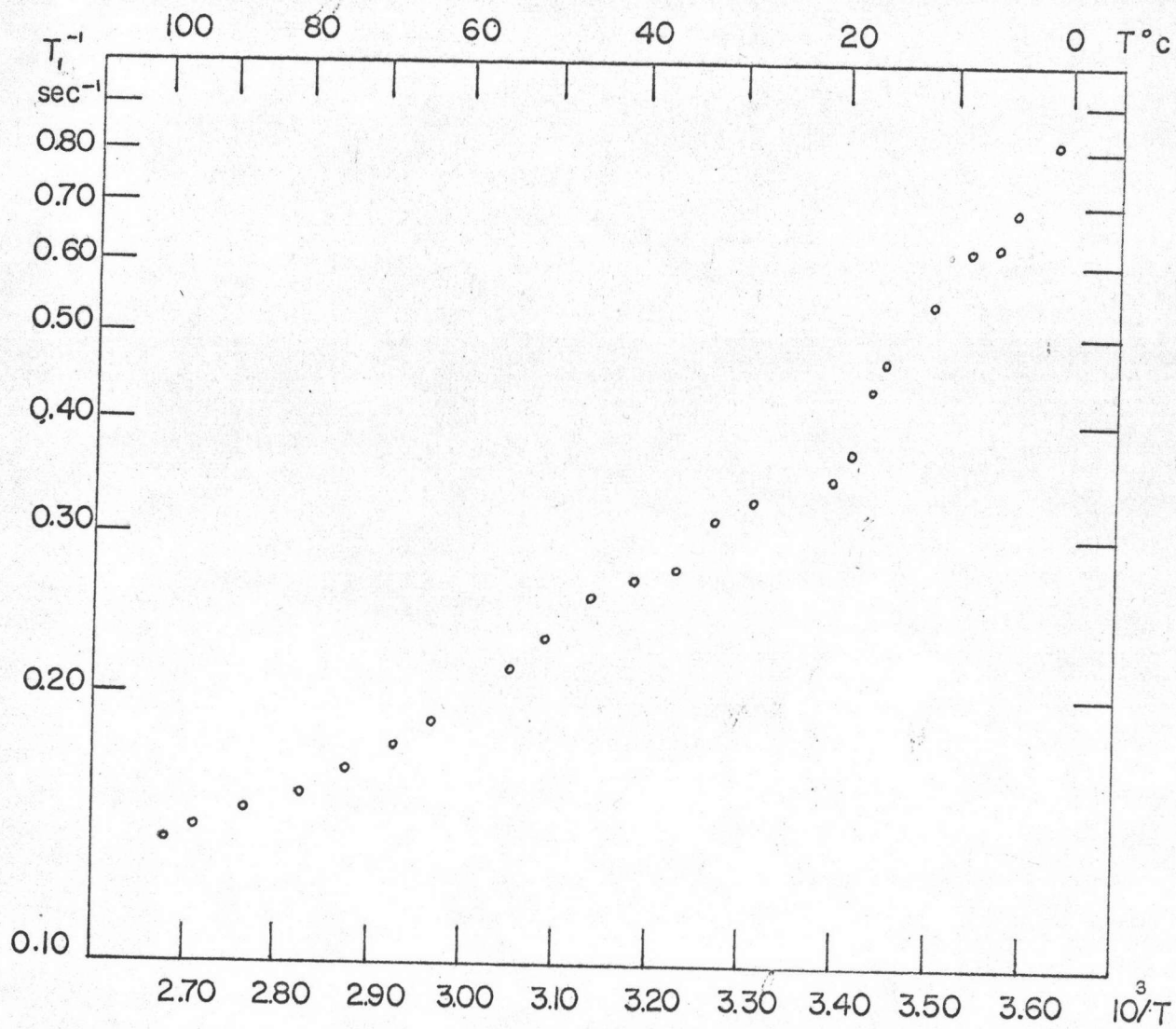


Fig. 4.1 Plot of  $\log(T_1^{-1})$  against  $10^3/T$

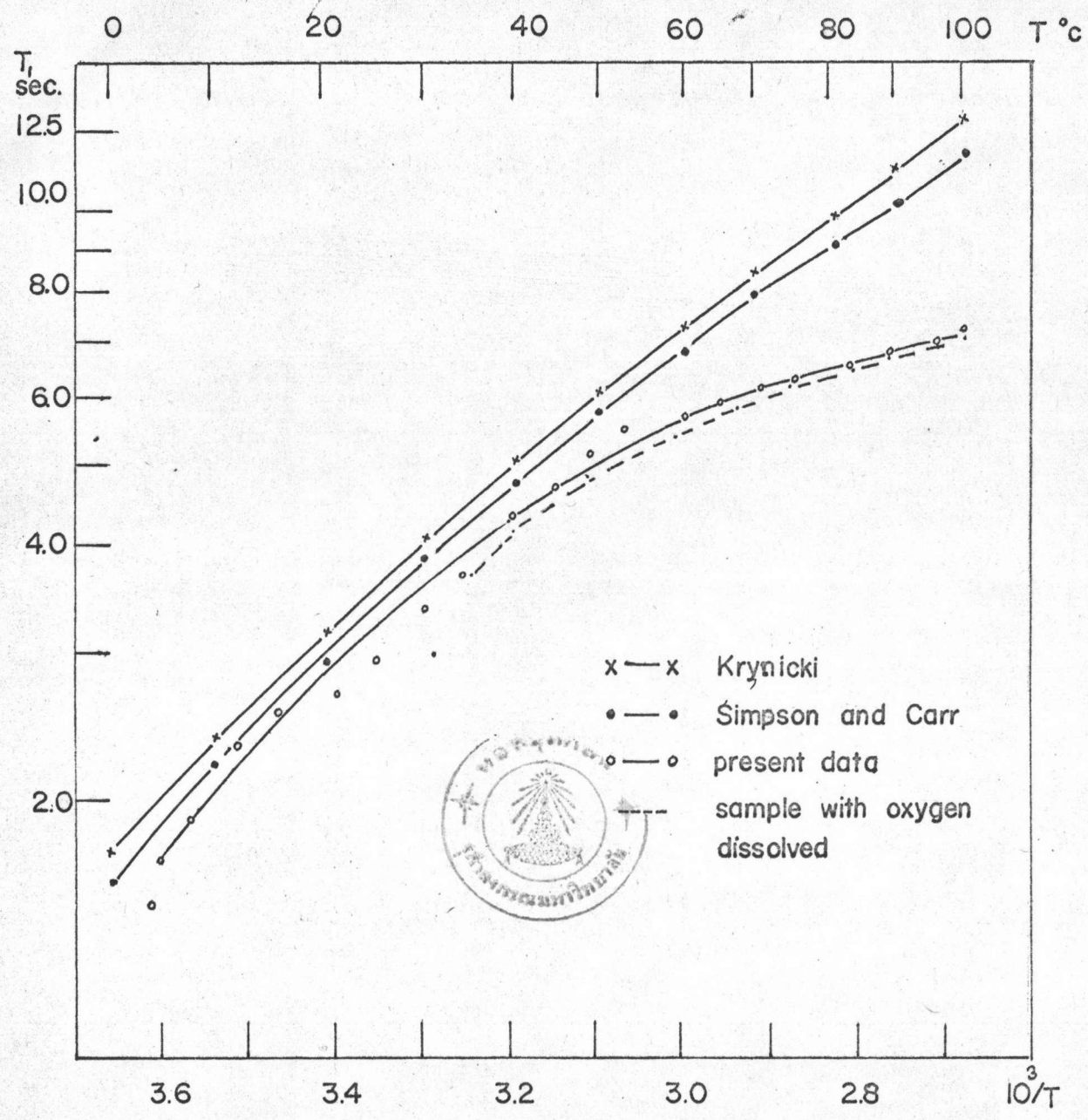


Fig. 4.2 Plot of  $\log(T_i)$  against  $10^3/T$

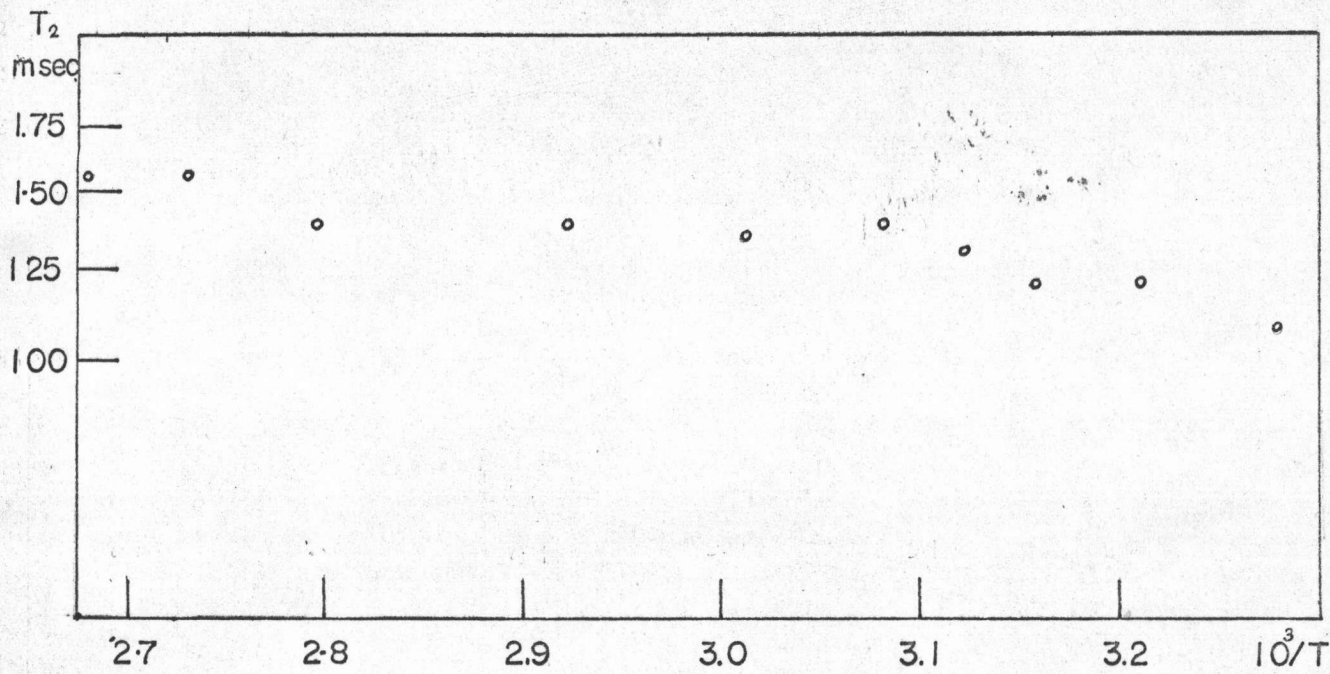


Fig. 4.3 Plot of  $\log(T_2)$  against  $10^3/T$

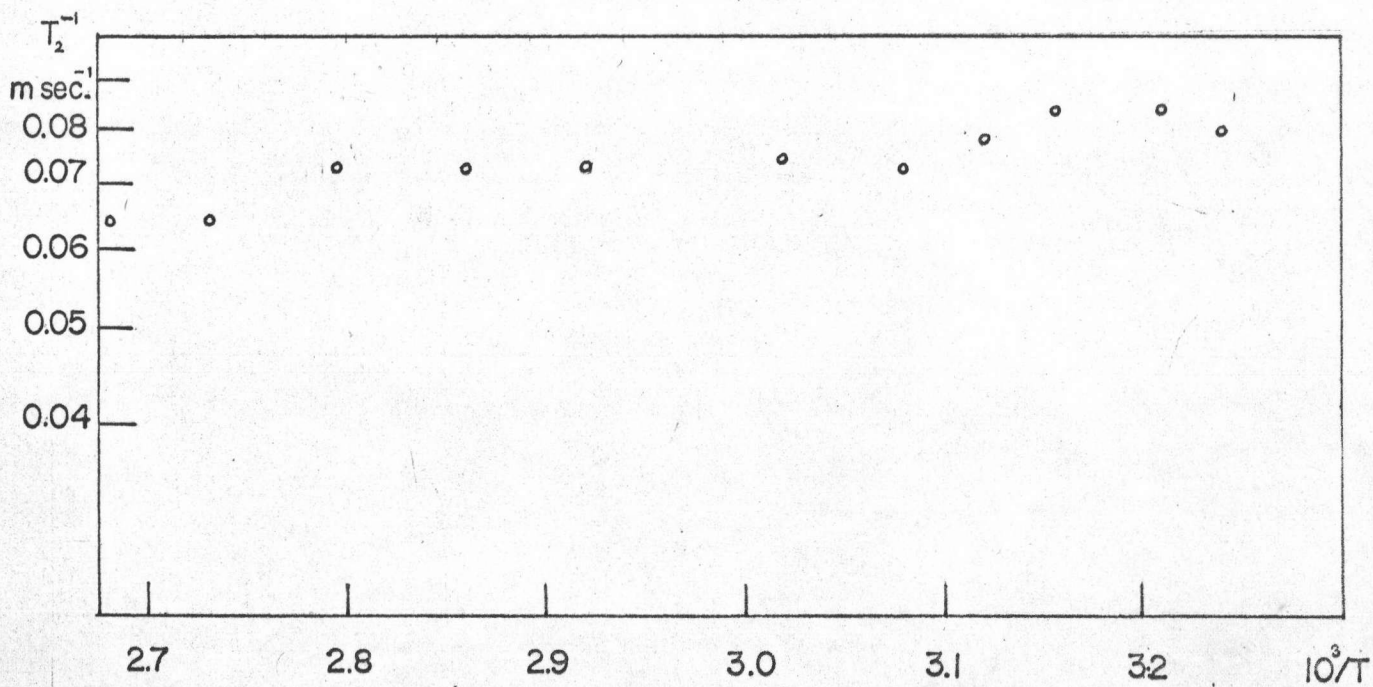


Fig. 4.4 Plot of  $\log(T_2^{-1})$  against  $10^3/T$



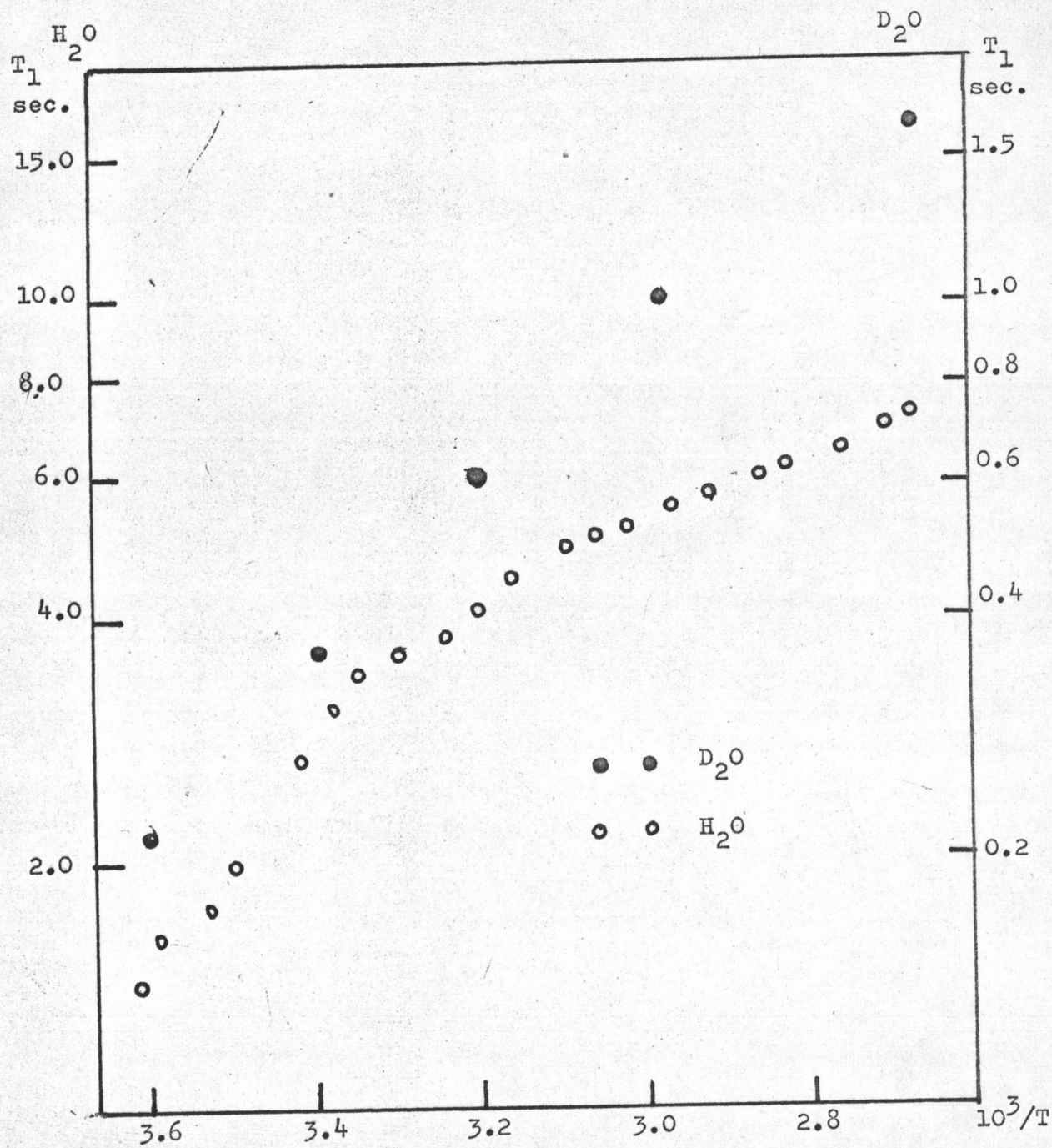


Fig. 4.5 Comparison of present values with  $D_2O$  values from Hindman, J.C.etal.

TABLE I

Temperature dependence of the spin-lattice relaxation time ( $T_1$ )\*

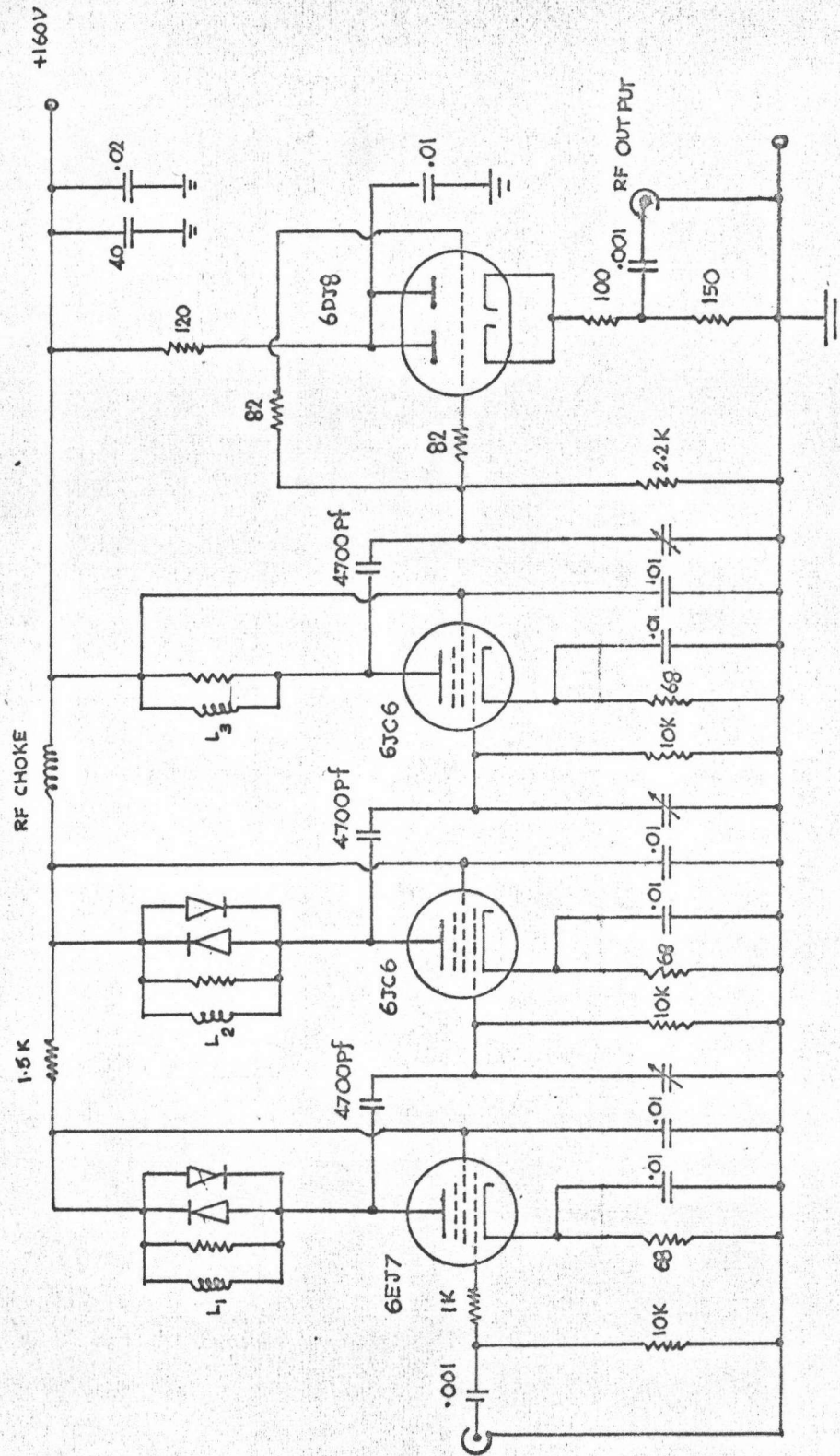
<u>January 19, 1972.</u>		<u>January 23, 1972.</u>		<u>January 24, 1972.</u>	
sample sealed in		$T_1$ °C	$T_1$ sec.	T (°C)	$T_1$ sec.
vacuum		100	7.5	100	7.2
T (°C)	$T_1$ (sec.)	97	7.4	96	6.9
100	7.4	92	6.9	89	6.5
96	7.1	84	6.8	83	6.3
90	6.8	77	6.7	77	6.0
85	6.7	71	6.5	70	5.7
80	6.5	65	6.2	64	5.4
76	6.4	60	6.0	59	5.2
67	6.1	52	5.5	52	4.9
61	5.9	47	5.2	45	4.5
53	5.4	40	4.3	41	4.2
48	5.1	36	3.8	36	3.8
40	4.6	29	3.4	31	3.6
36	4.3	22	2.9	28	3.5
33	3.8	17	2.3	23	3.1
30	3.5	14	2.2	20	2.7
26	2.9	10	2.0	18	2.4
21	2.6	7	1.8	13	2.0
18	2.5	5.6	1.5	10	1.8
13	2.0	4	1.5	6.6	1.6
8.4	1.7	3	1.4	3	1.4
4.4	1.5				

\* Estimated error  $\pm$  10 %



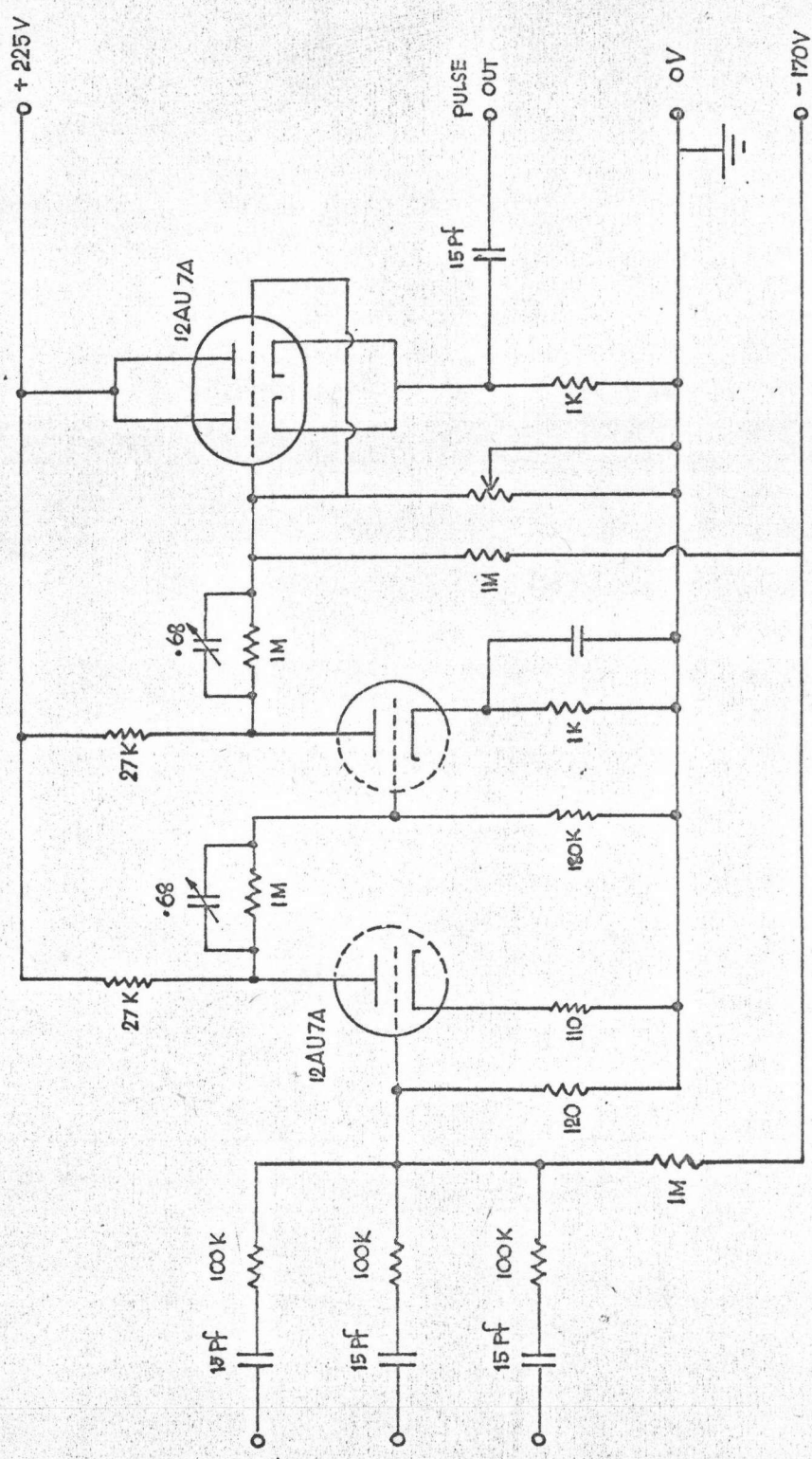




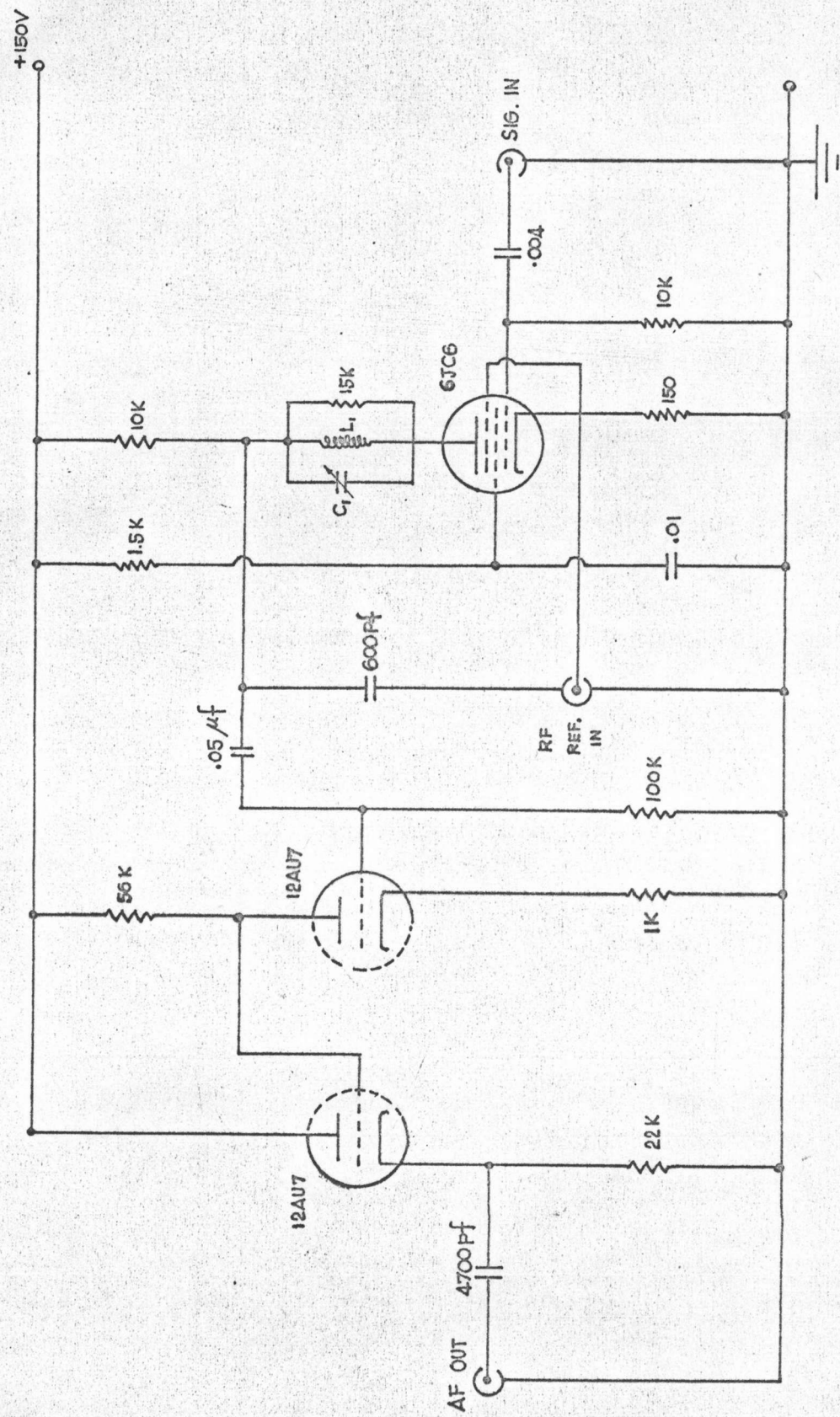


Appendix I.B RF. amplifier

I165b40a1

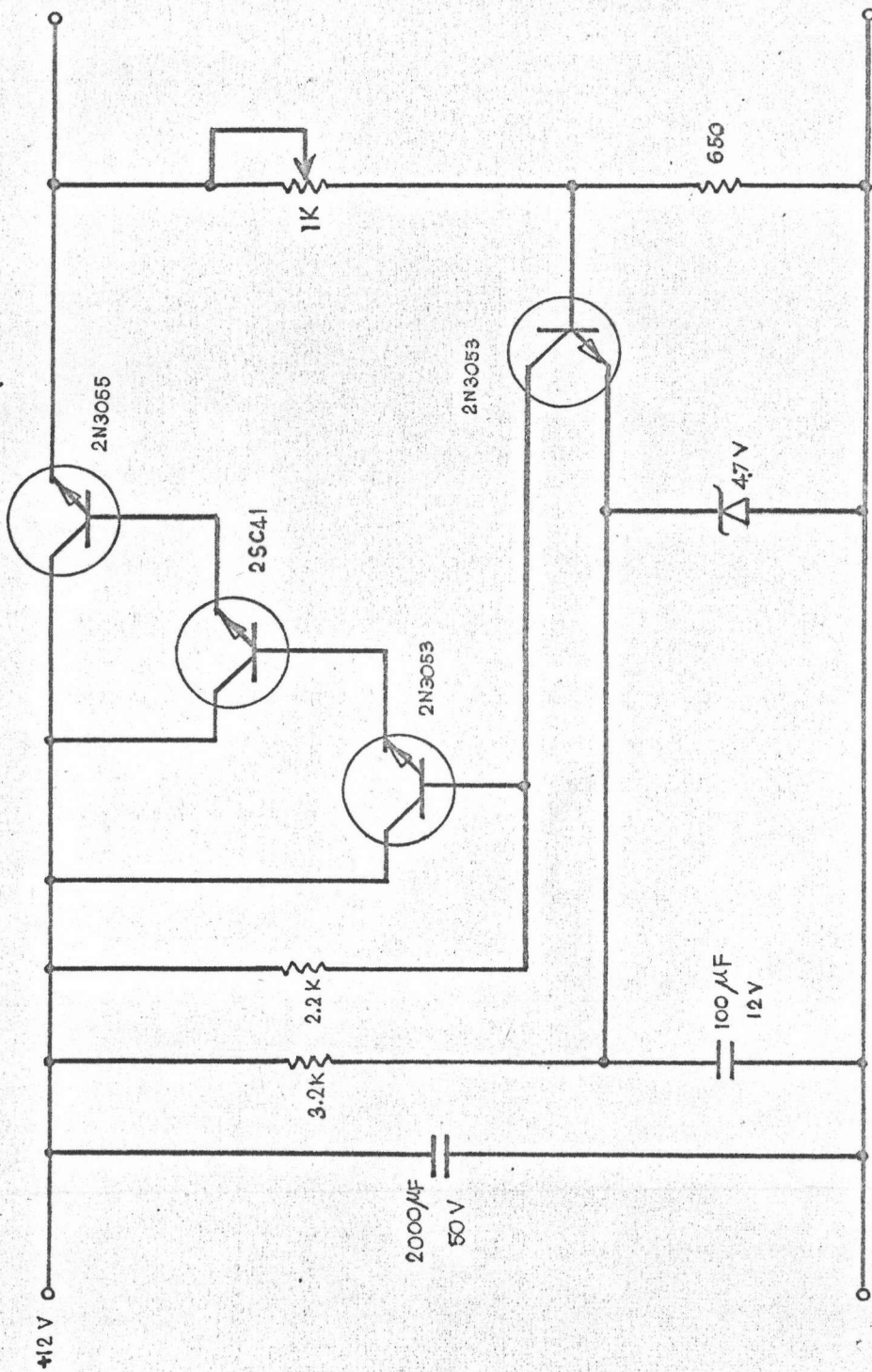


Appendix I.C Pulse amplifier



Appendix I.D Phase sensitive detector





Appendix I.E Regulated power supply