CHAPTER THREE

ELECTROLUMINESCENCE

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3-1 INTRODUCTION:

Electroluminescence (EL) is the phenomenon of light emission by luminors due to the sole action of electric field (a.c. or d.c.). Studies of the voltage, frequency and temperature dependance of time averaged electroluminescent brightness and the brightness wave forms are important means to understand the mechanism of electroluminescence. In the present chapter are described the studies on voltage and frequency dependance of the time averaged electroluminescent brightness, so as to gain information about the following aspects of electroluminescence.

i) Effect of activator on EL behaviour;
ii) Voltage dependance of EL brightness;
iii) Frequency depdndance of EL brightness;
iv) Mechanism of electroluminescence;
v) Brightness-current and current-voltage characteristics; and
vi) Insight into the recombination kinetics involved in EL process.

3-2 THEORETICAL BACKGROUND:

3-2.1 Relation between Brightness and Applied Voltage:

Electroluminescence brightness depends on the exciting voltage. A great variety of mathematical forms proposed by various workers, since the time of Destriau, are presented in the following few lines and there appears to be a considerable disagreement as regards the exact quantitative relationship.

Destriau (1), in year 1936, observed that the time average of the emission intensity of electroluminescent zinc sulphide phosphor increases exponentially with increasing amplitude of exciting alternating field. The first relation proposed by him is

$$B = a \exp. ({}^{-b}/_{V}), \qquad ---- \qquad (3.1)$$

where B and V are brightness and voltage respectively and a and b are constants, independent of V but dependent on temperature, type of phosphor and frequency of applied voltage. The relation is amenable to simple theoretical interpretation(2). Later, Destriau (3) changed this to,

$$B = aV^{n} \exp. (- b/V), \qquad ---- \qquad (3.2)$$

With n being a constant, the most probable value of which is found to be 2. The equation was originally reported as valid for microcrystalline ZnS phosphor and was in accordance with the findings of Gobrecht and his co-workers (4).

For single crystal of ZnS, a relation

$$B = aV^{n} \exp. (- b/\sqrt{V}) \qquad ---- \qquad (3.3)$$

is given by Alfrey and Taylor (5). This equation with $n = 1$ is found to hold good for electroluminescent ZnS:Mn films (6).

The equation (3.3) given by Alfrey and Taylor with $n = 0$ reduces to,

$$B = a \exp. \left(- b/\sqrt{V} \right) \qquad ---- \qquad (3.4)$$

This equation was first employed by Alfrey and Taylor (5) and Zalm et. al (7,8). Zalm and his co-workers (7,8) have reported that this equation is valid over seven decades of brightness for microcrystalline ZnS phosphors.

Later on Thornton and others (9,10,11) have shown that the equation (3.4) holds only at low voltage but that at high voltages the equation,

$$B = a \exp. \left(- b/V \right) \qquad ---- \qquad (3.5)$$

(Equation 3.2 with $n = 0$) works more satisfactorily.

Lehmann (12) found the emission of individual particles to obey equation (3.5) and showed that summation of the output of large number of particles leads to the normally observed equation (3.4). He thus considered the equation (3.5) to be the basic one for the electroluminescence, while equation (3.4) as resulted from a statistical effect in powders.

A relation similar to equation (3.5), viz.,

$$B = a \exp. \left(-b/_{V} + V_O \right) \qquad ---- \qquad (3.6)$$

was first proposed by Destriau and Ivey (13) and subsequently used by Morehead (14) with some success in ZnS and ZnS:Cu,Cl.

For microcrystalline ZnS activated with Cu, Howard et.al (15) and Lehmann (16) proposed:

$$B = aV \exp.\ (- {}^{b}/_{V} + V_o) \quad ----- \quad (3.7)$$

Where b ~~a~~and V_o increase slowly with frequency.

On the basis of exhaustion barrier theory, Taylor (17) deduced the following relation.

$$B = B_o \exp.\ [- ({}^{V_o}/_{V})^{1/2}] \quad ---- \quad (3.8)$$

Whereas on the basis of impac~~t~~ ionisation mechanism, Nagy (18) derived the following relation $B = a \exp. (-b/(1+cV)^2)$ ---- (3.9)
Luyckz and Stockking (19) reported a relation,

$$B = a \exp.\ (bV) \quad ---- \quad (3.10)$$

for microcrystalline ZnS;Mn. The equation was found to be valid over two decades of brightness, under alternating excitation.

Harman and Raybold (20) have suggested the power l~~o~~w relation,

$$B = a (V - V_o)^n \quad ---- \quad (3.11)$$

for ZnS phosphors with n = 3. A similar equation with $V_o = 0$, and n = 2.5 was given by Diemer (21) for single crystals of ZnS and was found to be valid at high voltages over five brightness decades. Halsted and Kollar (22) used the equation (3.11) with $V_o = 0$ and n = 7 through seven decades of brightness while Zalm et al. (23) used it with n = 3.5; with n = 2 was used by Piper and Williams (24) which holds good at high voltages. Recently, Gour and Ranade (25) used the equation (3.11) with $V_o = 0$ and n = 6.5 for CaS:Ag phosphors and Rastogi and Mor have reported a value of n around 5.7 for CaS:Nd, Cu phosphors (26).

On the basis of Piper and Williums theory, Howard et al. (15) obtained another relation as,

$$B = aV^{3/2} \left(1 - \frac{3V^{1/2}}{C} \right) \text{exp.} \left(\frac{-C}{V^{1/2}} \right) \quad - - \qquad (3.12)$$

with a and C constants.

It can be shown from impact ionisation theory (2) that the EL brightness (B) is related to the electric field (E), by

$$B = m \ \text{exp.} \ (-n/ E) \qquad - - - - \qquad (3.13)$$

Where m and n are constants.

If E is proportional to V (applied voltage) the equation (3.13) becomes

$$B = C \ \text{exp.} \ (- d/_V) \qquad - - - - \qquad (3.14)$$

Where C = m and d is another constant proportional to n.

Vlasenko and Popkov (27) have found another expirical formula for film panels, viz.

$$B = g \ \text{exp.} \ \left(\sqrt{V/_h} \right) \qquad - - - - \qquad (3.15)$$

Chan and Yu (28) have shown that EL emittance of film panels depend on various parameters such as composition and aging of panel and applied voltage. They have studied evaporated film panels of ZnS:Mn, Cu, Cl and have given an emirical formula to describe voltage dependance of EL emittance as

$$B = A \ \text{exp.} \ \left(- G/ \ (F + \sqrt{V}) \right) \qquad - - - - \qquad (3.16)$$

Where A, G and F are functions of operating time and can be regarded as constants during any measurement of EL emittance. In the initial period, when $F \gg \sqrt{V}$, the equation reduces to equation (3.15) while in the final stages of operation, when $F \ll \sqrt{V}$, the equation reduces to equation (3.4). Thus theory may be regarded as a first step towards establishing a second theoretical basis for field dependance of EL emittance.

Recently Z. Porada (29) applied the EL model suggested by Alfrey and Taylor (30) to explain the observed EL emission excited by high energy electrons in the strong electric field of the metal semiconductor junction and arrived at an equation of the form,

$$B = \gamma \exp.\left(- \frac{\gamma \pi}{2 W} \right) \exp.\left(-\alpha / \sqrt{V} \right) \; - - - \quad (3.17)$$

Which may be written as,

$$B \doteq B_o \exp.\left(- A/f \right) \exp.\left(- \alpha / \sqrt{V} \right) \; - - - - \quad (3.18)$$

In equation (3.18), B_o is a constant independent of units in which B is expressed, A is a parameter dependent on the technological conditions under which samples are prepared and temperature, f is the frequency, α is a parameter dependent on the value of the critical intensity of the electric field causing ionisation of the luminescent centres with V as the applied voltage.

3-2.2 Relation Between Brightness and Applied Frequency:

When a powder dielectric cell is excited with a sinusoidal voltage, a continuous emission of light is observed. The magnitude of brightness is found to be a function not only of the applied voltage but also of the frequency. Various relations between brightness and frequency given by different workers are summarised below.

Curie (31,32) has derived a theoretical expression on the assumption that there exists a bimolecular process of recombination of electrons with luminescence centres and, that the same number of excited centres are produced per cycle. The expression is

$$B = B_0 \frac{n_0^2 \alpha}{\left(1 + \frac{n_0 \alpha}{2f}\right)} \quad ---- \quad (3.19)$$

Where α is the recombination coefficient defined by $dn/dt = -\alpha n^2$, n being concentration of electrons in conduction band at time t, n_0 is the initial concentration of free electrons in the conduction band, f is the frequency of applied voltage and B_0, a proportionality constant. In a simple form, the above relation may be written as

$$B = S \,/\, (1+K\, (\alpha S)^{\frac{1}{2}} \,/\, f\,) \quad ---- \quad (3.20)$$

Where K is a constant, α, the recombination coefficient, S, the saturation output for high frequency. The relation predicts that a higher frequency is required to approach saturation at higher voltages.

Thornton (9) considering the recombination rate as determined from the electrons released from traps and controlled by electric field obtained

$$B = N_o f \left[1 - \exp. \left(- {}^{A}/_{f} \right) \right] \quad ---- \quad (3.21)$$

Where No is the number of excited centres for each half cycle, assumed to be constant.

$$A \simeq \int_{0}^{2\pi} \exp. \left(aV \operatorname{Sin}x \right) dx$$

with $x = \omega t$ is a field dependent factor which increases with voltage. Generally, brightness changes linearly with frequency and tends to saturate at higher frequencies whereby equation (3.21) can be approximated to $B = N_o A$.

Alfrey and Taylor (30) has given a relation

$$B = B_o p \exp. \left({}^{-P}/_{4f} \right) \exp. \left({}^{C}/_{\sqrt{V}} \right) \quad ---- \quad (3.22)$$

With C as a constant, V being the applied voltage, P the rate constant for thermal emptying of traps and is given by

$$p = S \exp. \left(- {}^{E}/_{kT} \right) \quad ---- \quad (3.23)$$

Here S and E represent the frequency factor and the trap depth respectively. The equation (3.22) is, however, found to be inexplicable for the variation in the brightness-frequency characteristics; with the applied voltage and disagrees with the empirical results at lower temperature (33).

Zalm (34) showed that the light emission during each cycle of the applied voltage is not constant, but is dependent on frequency of the applied field. He gives a relation

$$B \propto \exp. \left(- \text{constant} / \sqrt{V} \right) \quad ---- \quad (3.24)$$

Wherein $V = F(f, t)$, f being frequency and t the time.

Thus, light emitted for a cycle is inversely proportional to f, so that the total light emitted per unit time is independent of frequency, which is contrary to the observation.

Zalm considers that the actual voltage across the EL cell governed by extra capacitance (C) and resistance (R), present in the experimental cell. Thus for a series of capacitor C and the resistance R, the actual voltage across the cell is given by

$$WRC\,V_0 \Big/ \sqrt{1+W^2R^2C^2} \qquad ---- \quad (3.25)$$

Where V_0 is the amptitude of the applied voltage to the whole system of capacitor and EL cell. If $RC \gg \frac{1}{\omega}$, the voltage across the cell and consequently the luminous emittance is independent of frequency, while with $RC \ll \frac{1}{\omega}$ the emittance increases more than linearly with the frequency. It is thus possible to describe any frequency dependance with a suitable distribution in RC values of the system.

Johnson, Piper and Williams (35) deduced the brightness-frequency relation by considering both excitation and recombination processes. By denoting the relaxation time of the excited electrons returning to empty luminescence centre by τ_1 and time constant of creation of primary electrons by τ_2 , Johnson et al. found

$$B \propto [1-a(1-\exp.(-{}^{1}/_{2f\tau_2})\ \exp.({}^{-1}/_{2}\,f\tau_1)\,] \qquad (3.26)$$

Where a is a constant. This equation does not explain the applied voltage dependance of the brightness-frequency characteristics (35).

Morehead (36), considering the transit time of carrier electrons from the higher intensity region of the field to the lower one, suggested a relation

$$B \propto (1-\exp. (-\mu)) \qquad ---- \quad (3.27)$$

where

$$\mu = (aV/f^{0.6}) \exp. (-E/kT) \qquad ---- \quad (3.28)$$

In order to have a good agreement with the experimental results, he assumed the electron mobility to be proportional to the o.6th power of the frequency; but this assumption has no physical justification (33).

Chan and Yu (28) have empirically suggested that the EL emittance (B) varies with frequency (f) of applied sinusoidal field as

$$B = B_s - B_m \exp. (-f/fc) \qquad ---- \quad (3.39)$$

where B_s, B_m and f_c are constants ($B_s \neq B_m$). The equation indicates that B approaches a saturation value B_s when $f \gg f_c$ and a linear relation between B and f when $f \ll f_c$.

3-2.3 Brightness Waves:

The variations in the EL brightness with time, during the applied alternating fields are called 'Brightness waves'. Besides, it is a graphic indication of phase relationship of light component (applied to Y- plates) to the impressed voltage (applied to X-plates) on a double beam cathode ray oscilloscope. The shape of the brightness wave depends upon the field intensity, the frequency and the direction in which the light output is observed. It also depends upon the nature of activator, co-activator and on the spectral characteristic of the detector (PM-tube) too. The existence of brightness waves and the fact that their frequency is twice the frequency of the applied voltage were first reported by Destriau (37),(38) in year 1937.

3-2.4 Efficiency of Electroluminescence:

The lumineous efficiency (lumens/Watt) of electroluminescence of powdered crystal phosphors embaded in an insulating medium and excited by alternating fields depends on the quality of the phosphor, the details of the EL-cell design and the conditions of excitation.

Lehmann (39) has given an empirical relation for efficiency of an EL phosphor, namely,

$$\eta^2 = C^2 \quad (B/V^4) \qquad - - - - \qquad (3.30)$$

Where C is a constant. According to this equation, efficiency increases so long as the brightness increases faster than the fourth power of the applied voltage and not on the rate of change of voltage (40).

The simple calculations of luminescence efficiency, η, in terms of brightness units (arbitrary), as a function of applied voltage and frequency are possible using Lehmann's(39) relation, viz,

$$\eta = \frac{B}{W} = \frac{B/f}{aV^2 \; (K''_o \; = b \; ({}^{B}/{}_{f})^{1}/{}_{2}} \qquad - - - - \qquad (3.31)$$

Where K''_o , a and b are constants. The values of a and b are to be taken from the work of Schwertz et al. (41) while K''_o is taken to be unity.

3-3 RESULTS AND DISCUSSION:

Studies of voltage and frequency dependence of EL brightness have been carried out in the voltage range of 0 volts to 1500 Volts$_{rms}$ and frequency range of 50 Hz to 2000 Hz.

3-3.1 Voltage Dependence of EL Brightness:

The EL brightness B (in arb. units) is plotted as a function of applied voltage V (in Volts r.m.s.). Some representative curves for various samples at different frequencies are shown in fig. 3.1. From the figure it is clear that the increase in EL brightness is sharper at higher voltages than at lower ones, and linear relationship between them does not hold well. Moreover, the threshold voltage--the voltage above which EL emission starts-is found to be greater than 350 Volts, for all the samples. From the table 3-1 it may be seen that the threshold voltage first decreases and then increases with activator concentration.

The nature of the possible relationship existing between brightness (B) and applied voltage (V) is estimated by plotting different graphs, based on number of empirical relations, viz., (1) log B versus V (ii) log B versus log V (iii) log B versus $\frac{1}{V}$ (iv) log B versus $\frac{1}{\sqrt{V}}$ (v) log $\frac{B}{V}$ versus $\frac{1}{V}$ (vi) log $\frac{B}{V}$ versus $\frac{1}{\sqrt{V}}$. It is observed that, out of these plots, the plots between log B and log V and log B and $^1/\sqrt{V}$ are closely linear showing slight deviations from main plots at high voltages.

Some of the typical plots between log B versus log V are shown in Figs. 3.2 - 3.4 for various samples, obtained at different frequencies. It may be seen from these figures that the curves are closely linear showing the bending towards the voltage axis at high voltages. The bending starts at relatively low voltages (except for samples P_3 & P_9) for higher frequencies of applied field, indicating thereby the saturation of brightness to occur at low voltages. The linearity between log B and log V suggests that the power law relation of the form (25),

$$B = aV^n \qquad ---- \qquad (3.32)$$

with a and n being constants, to exist over the observed region of linearity. The relation is similar to equation (3.11) with $V_0 = 0$. The power law relationship between brightness and voltage has also been observed by Gour (42) for CaS:Ag phosphor and by Lawangar et al. for CaS;Bi;Pd phosphors (43).

The value of n in equation (3.32) was evaluated by the method of least squares (44) using the relation,

$$n = \frac{\Sigma X \, \Sigma Y \; - \; N \, \Sigma X \cancel{x} Y}{(\Sigma X)^2 \; - \; N \, \Sigma X^2} \qquad ---- \qquad (3.33)$$

Where X - log V and Y = log B and N being the number of observations. The n values thus obtained are listed in Table 3.2 and vary from 2.00 to 6.35. The variation is not systematic in character with activator concentration.

Besides the power law, a relation proposed by Zalm et al (7,8), viz.,

$$B = a \exp. \left(- {}^{b}/\sqrt{V} \right) \qquad ---- \qquad (3.4)$$

with a and b as constants, is also found suitable over a limited range of voltages. Such an exponential dependance of brightness on voltage was observed by Wachtel (45) for CaS:Cu,Eu phosphors, by Laud and Kulkarni (46) for SrS:Cu phosphors and by Patil for CaS:Ag, Dy phosphors (47). According to equation (3.4) a plot of log B versus ${}^{1}/\sqrt{V}$ is a straight line. Some of such plots are shown in Figs.3.5 to 3.7. The plots are seen to be nearly linear over a limited range of voltage and show bending at high voltages.

The results of voltage dependance of brightness observed in present investigation are similar to those reported by Rastogi and Mor (26) on CaS:Nd:Cu phosphors; by Masoorkar and Ranade (48) on SrS:Cu phosphors and by Patil (47) on CuS:Ag, Dy phosphors. Rastogi and Mor reported that the relation (3.32) is more suitable for their samples than the equation (3.4).

The simultaneous validity of these two equations is suggested by Masoorkar and Ranade (48).

The binding of the plots at high voltages was also observed by Rastogi and Mor (26). It might be due to one or more of the following reasons:

i) the loss of voltage in conducting electrodes thereby lowering the field strength at high voltages,

ii) the traps cannot be emptied as fast they are filled at high frequencies and give rise to space charge scattering and hence an increase in the radiationless transitions at higher fields,

iii) the distribution of the applied a.c. voltage in a micro-crystaline powder form of phosphors.

Lehmann (49) has determined the distribution function for the grain size in an actual sample and have shown that the plot of log B versus $1/\sqrt{V}$ is a straight line which bends for high voltages.

3-3.2 Frequency dependence of EL Brightness:

Some representative plots illustrating the frequency dependence of EL brightness (log B as a function of log f) at various voltages are shown in Fig.3.8 to Fig.3.10. The results obtained can be summarised as;

i) At low frequencies, the brightness decreases more rapidly with increase in frequency.

ii) At lower voltages, the decrease in brightness with frequency is more rapid than that at higher voltages.

iii) At higher frequencies and lower voltages, the brightness becomes independent of frequency, while at higher frequencies and higher voltages it decreases more or less linearly with increase in frequency.

In most of the studies on frequency dependence of EL brightness, it is observed the EL brightness increases more or less linearly with increase in frequency (9,28,31,32,47). However, a few workers have reported the decrease of EL brightness with increase in frequency (50,51). The dependence of EL brightness in the present study is very similar to that reported by Piero et al. (50). The decrease of EL brightness with increase in frequency cannot be accounted for on the basis of simple physical models (50). It involved much theoretical complications (51) and rather troublesome questions (50). A probable cause of decrease of EL brightness with increase in frequency lies in the decrement of voltage across the EL cell with increase in frequency due to a spurious frequency dependence of dielectric constant of the phosphor at low frequencies (52). However, in the present investigation this probability was removed by adjusting the voltage across the EL cell to the required constant value.

Though there is no satisfactory theory to explain the decrease of EL brightness with increase in frequency, the frequency independent EL brightness observed at higher frequencies and lower voltages can be explained on the basis of the theories proposed by Thornton (9) and Curie (31,32). At moderately high frequencies the equation (2.21) approximates to $B = NoA$. As No is a function of applied voltage, the equation predicts the effect of voltage on frequency dependance of EL brightness. Moreover, the equation (3.19) given by Curie (31,32), at higher frequencies takes the form $B = B_on^2$. The expression is independent of frequency and points to the frequency independent EL brightness. However, the frequency independent EL brightness, in the present study, is not observed at higher voltages. This might be due to lying of this region well above the frequency region studied.

3-3.3 Electrical Characteristics of Phosphors:

A) Brightness- Current Characterstics:

The log-log plots of brightness (B) versus device current (I) under a.c. field excitation are shown in Fig.3.11 for some samples. The brightness B is seen to be an increasing function of current in initial part, but curves bend towards the current axis in latter part. In the initial region, the variation can be described by the relation of the form,

$$B \propto I^m \qquad ---- \qquad (3.34)$$

Where m is an exponent whose value depends upon the current region chosen. In the present case m varies from 3.2 to 4.8. The bending of the plots may be due to heating effect becoming apparent at higher current levels. As suggested by Park and Shin (53), the linear dependence of brightness on device current is often observed for radiative recombinations associated with high field impact ionisation process. The power law dependence of brightness on current ($B \propto I^m$) and exponential relation between brightness and voltage $[\, B \propto \exp. \, (^{-b}/\sqrt{V}) \,]$ indicates that the mechanism of EL process is likely to be an acceleration collision i.e. probability of impact ionisation is proportional to $\sqrt{V}$ in the Mott-Schottky barrier.

B) Current-Voltage Characteristics:

i) Under a.c. Field Excitation:

Fig.3.12 depicts the variation of device current with square root of applied voltage at different frequencies. It may be seen that the plots exhibit two distinct regions. The region towards the low voltage side closely follows the relation $I \simeq \exp. \, (a \sqrt{V})$ while the other, on high voltage side, obeys the relation $I \simeq \exp. \, (aV)$. (See Fig.3.13). The voltage at which slope of the curve decreases may be called as a change over voltage and is found to be different for different samples. The change in current voltage characteristics from $\exp. \, (a \sqrt{V})$ to $\exp. \, (aV)$ predicts the existence of an exhaustion barrier (54,55), the width of which increases as square root of applied voltage.

c) Relative Efficiency:

Fig.3.14 depicts the variation of brightness (B) with power (W=VI) supplied to the EL cell. It may be seen that the brightness increases with supply of energy, attains a maximum and then saturates. This might be expected (as explained earlier vide Section 3-3.1), due to increase in radiationless transitions at high voltage levels. The ratio ($^B/W$), termed as relative efficiency in arbitary units, is plotted as a function of W and it shows that with increase in energy the efficiency increases, goes through maximum and then decreases (Fig.3.14). Similar are the findings of Kulkarni and Ambardekar (56), Bhand (57) and Patil (47) who studied efficiency using Lehmann's relation (viz. equation 3.31).

3-3.4 Effect of Activator Concentration on Electroluminescence Behaviour:

It may be seen from Figs.3.1 to 3.10 that for various samples containing different concentrations of activator Zn, the nature of voltage and frequency dependence of brightness is almost similar. The electrical characteristics of the phosphors are also not affected sensitively by the concentration of the activator (Figs.3.11 to 3.14). However, when EL brightness is plotted as a function of Zn concentration (Fig.3.15 to 3.16), the EL brightness increases, attains a maximum and then decreases. Thus, it may be concluded that the activator does not significantly affect the EL behaviour of the phosphors but only the relative EL brightness.

3-3.5 Mechanism of Electroluminescence:

Excitation mechanism of EL is roughly classified into three models, viz.,

i) direct excitation by the electric field,
ii) impact excitation by the electrons accelerated in the strong field regions, and;
iii) injection of minority carriers through the P-n homojunction or heterojunction.

The qualitative test of prepared phosphor for thermoelectric power indicates that the phosphors are n-type, and as such the carrier injection mechanism for exciting the phosphor appears to be improbable. On the other hand, to observe the EL emission comparatively high fields are required. For all samples studied, the threshold voltage is found to be greater than 350 volts. r.m.s. The requirement of an intense electric field for EL emission to occur alongwith the existance of power law relationship between brightness and voltage suggests that the probable mechanism of excitation, in these phosphors, is likely to be direct field ionisation of either valence band electrons or impurity centres; where transfer of electrons into the conduction band takes place by a quantum mechanical tunneling process (58,42). However, the existance of relation $B = a \exp. (^{-b}/\sqrt{V})$, besides the power law, indicates that the luminescence emission also results from a potential barrier of Mott-Schottky type, where field is proportional to $\sqrt{V}$; and the mechanism of excitation is acceleration collision type (59,60). The electrical characteristics such as brightness-current, current-voltage also go in favour of existance of a potential barrier of Mott-Schottky type. Thus it may be concluded that the probable mechanism of EL in these phosphors is likely to be direct field ionisation of either valence band electrons or impurity centres, where transfer of electrons into the conduction band takes place by quantum mechanical tunneling process through the Mott-Schottky barrier, existing at the grain boundaries. These electrons recombine radiatively at a later stage with impurity centres or holes created in the valence band, giving emission.

3-3.6 Kinetics Involved in EL Process:

In the present investigation the existance of power law relationship between brightness and voltage indicates the possibility of bimolecular process in recombination of electrons with luminescence centres (25,26). However, besides the power law, the relation $B = a \exp. (^{-b}/\sqrt{V})$ is also found suitable over a limited range of voltages. Hence, here it cannot be concluded with reasonable certainity that the process of recombination of electrons with luminescence centres is bimolecular.

3-4. SUMMARY:

The important features of this chapter are to be summarised as follows:

1. The EL brightness B and applied voltage V follow the power law relation, $B = aV^n$, over a wide range of voltages. Besides, an exponential relationship $B = a \exp. (^{-b}/\sqrt{V})$, is found suitable over a limited range of voltages.
2. At lower frequencies, the brightness decreases rapidly with frequency. At higher frequencies the variation is almost linear.
3. The brightness-current and current-voltage characteristics predict the existance of Mott-Schottky type exhaustion barrier.
4. The activator Zn has no significant effect on the EL behaviour of phosphors, but it affects only the EL brightness.
5. The probable mechanism of EL in these phosphors is likely to be the direct field ionisation of either the valence band electrons or impurity centres, where

transfer of electrons into the conduction band takes place by quantum mechanical tunneling process through the Mott-Schottky barrier existing at the grain boundaries.

6. Some of the results indicate that the kinetics of EL process is likely to be bimolecular, but conclusion cannot be drawn with reasonable certainty.

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Table 3.1: Values of Threshold Voltages in volts for Different Samples at Different Frequencies:

Frequency in Hz Sample Number	500	1000	2000
P_1	950	990	1050
P_2	820	930	1010
P_3	790	800	970
P_4	780	780	930
P_5	650	740	900
P_6	600	660	820
P_7	580	625	730
P_8	430	540	675
P_9	350	410	560
P_{10}	380	450	625
P_{11}	425	510	690
P_{12}	470	570	730

Table 3.2: Values of n for Different Samples

Frequency in Hz —— Sample Number	500	1000	2000
P_1	2.74	2.36	2.09
P_2	4.69	4.15	3.88
P_3	3.25	2.94	3.96
P_4	5.52	2.39	5.00
P_5	2.73	3.04	3.14
P_6	4.11	3.75	4.18
P_7	4.26	4.58	5.73
P_8	3.79	2.05	4.81
P_9	4.21	3.23	4.75
P_{10}	6.35	3.90	5.11
P_{11}	3.90	3.55	2.00
P_{12}	5.38	4.85	4.59

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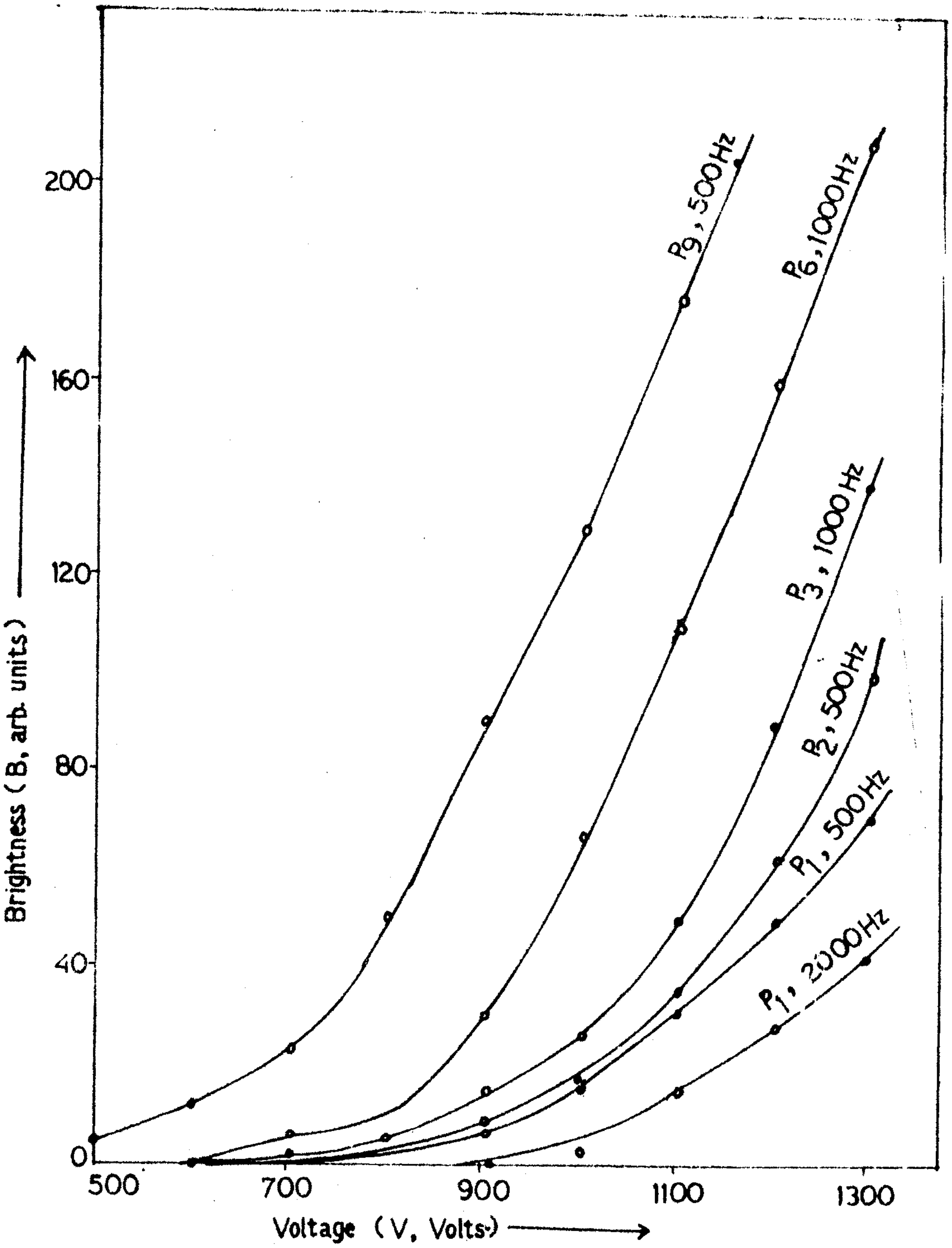

FIG. 3·1— PLOTS OF B Vs V FOR SOME SAMPLES.

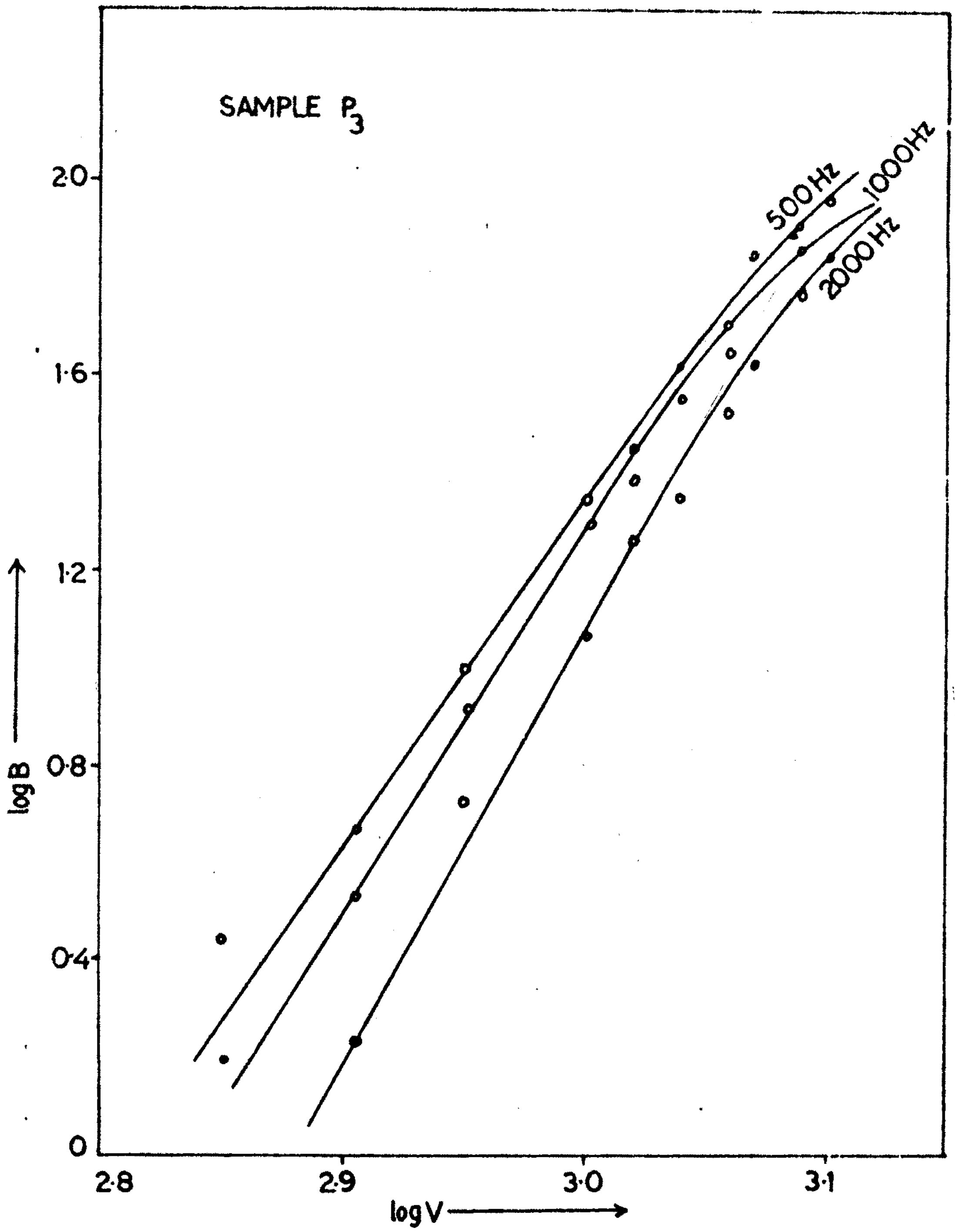

FIG. 3.2——PLOTS OF LOGB Vs. LOGV.

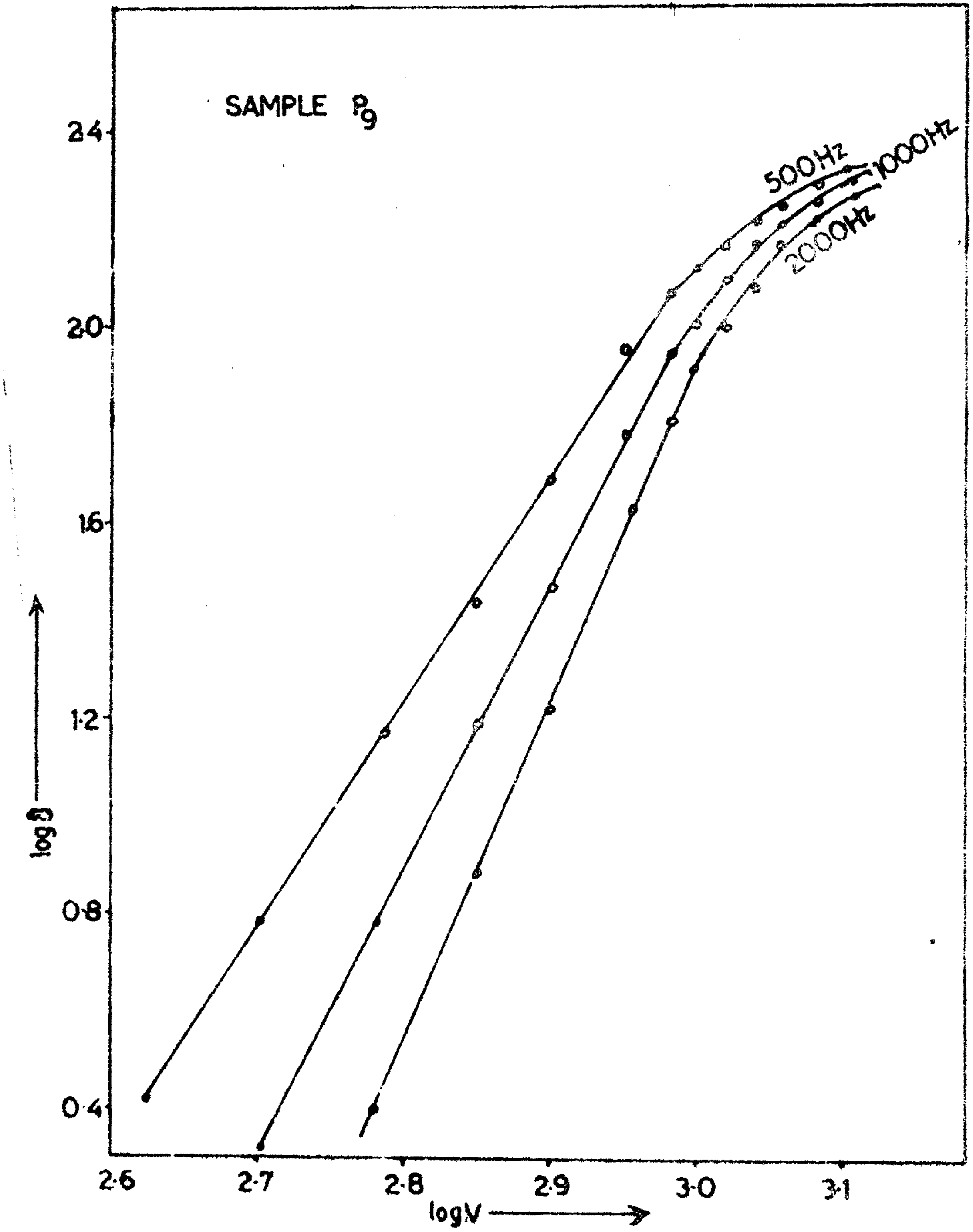

FIG. 3·3 —— PLOTS OF LOGB Vs LOGV.

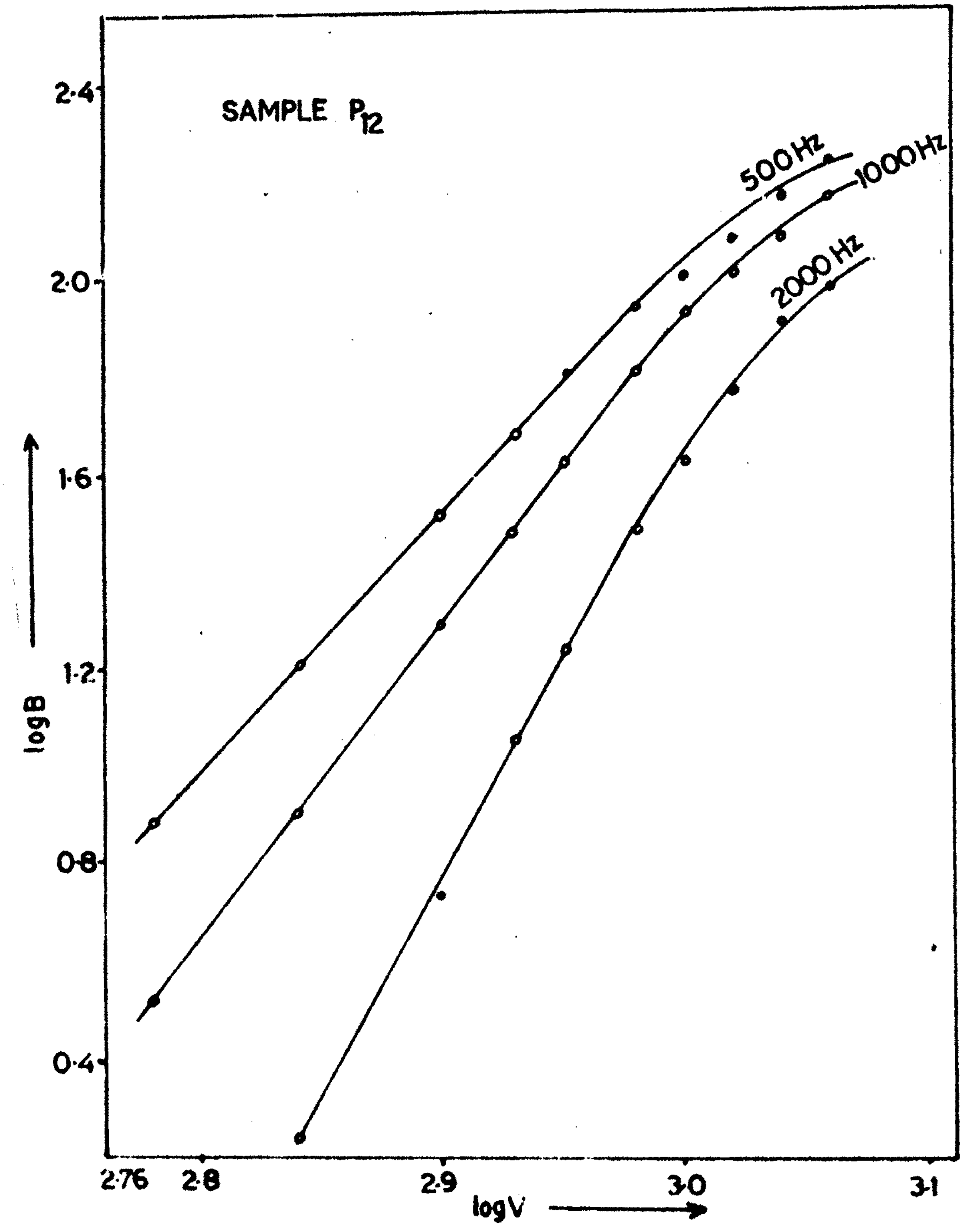

FIG. 3·4—PLOTS OF LOGB Vs. LOGV.

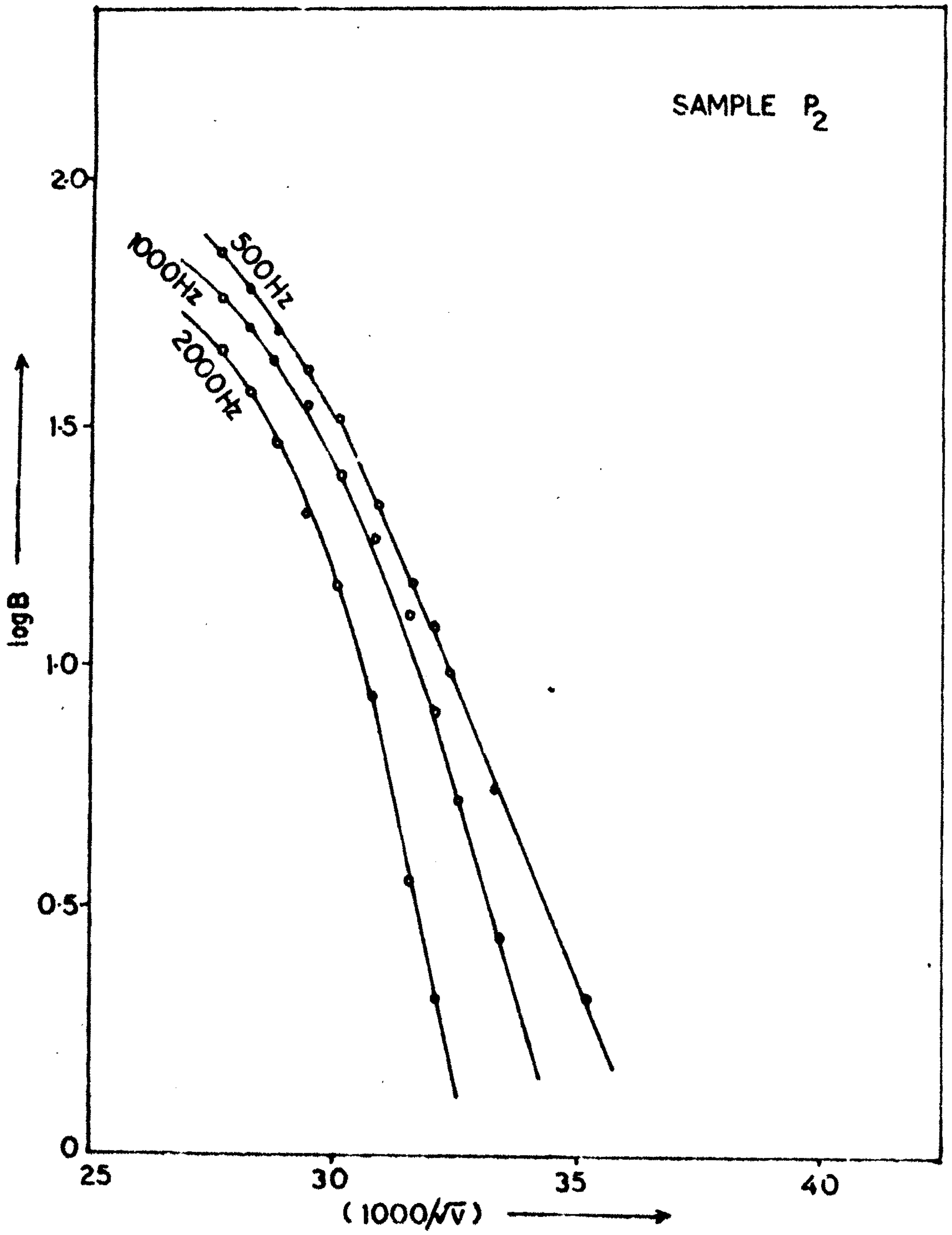

FIG 3.5—PLOTS OF LOGB Vs (1000/√V)

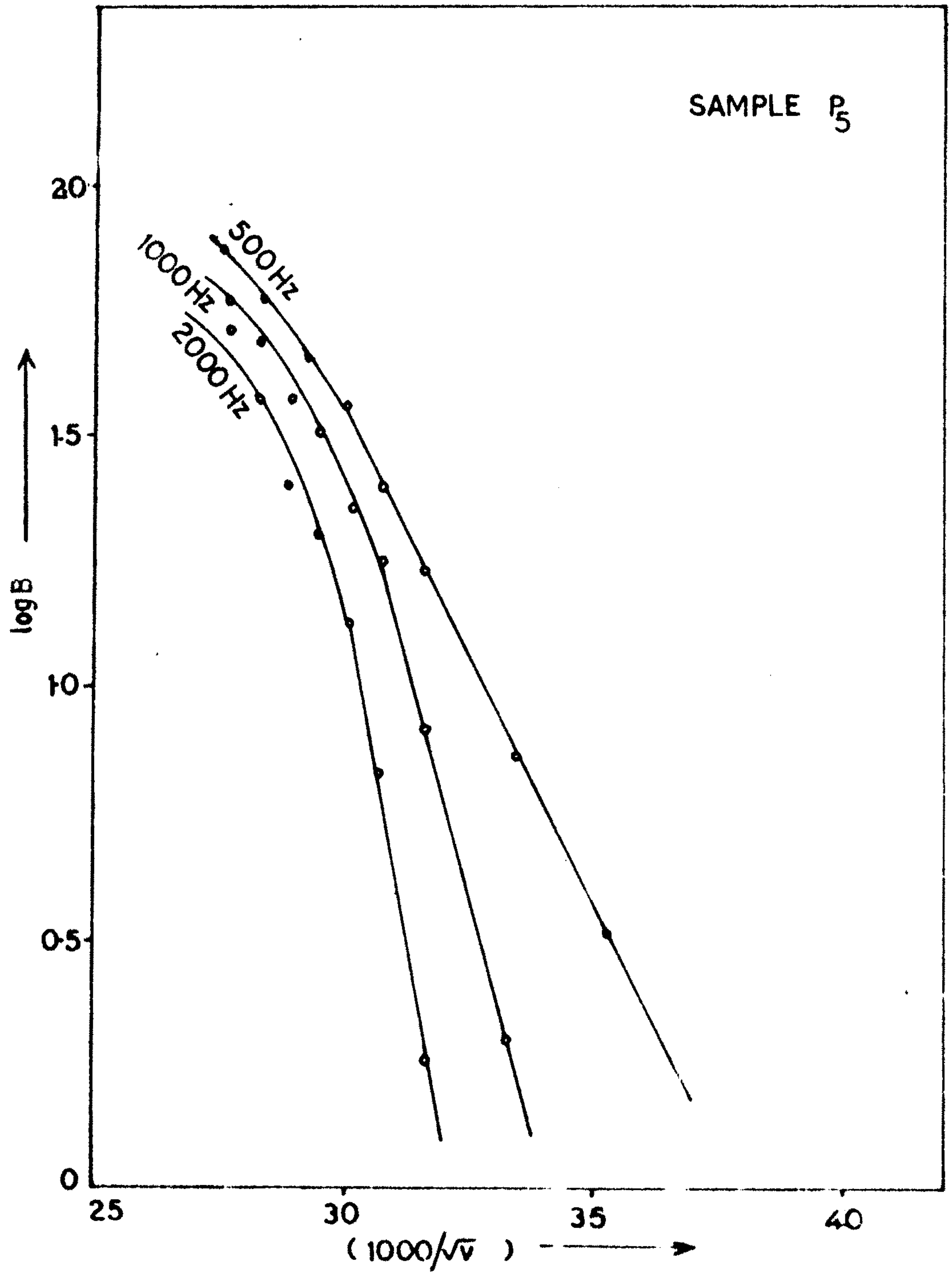

FIG. 3.6 PLOTS OF LOGB Vs (1000/√V)

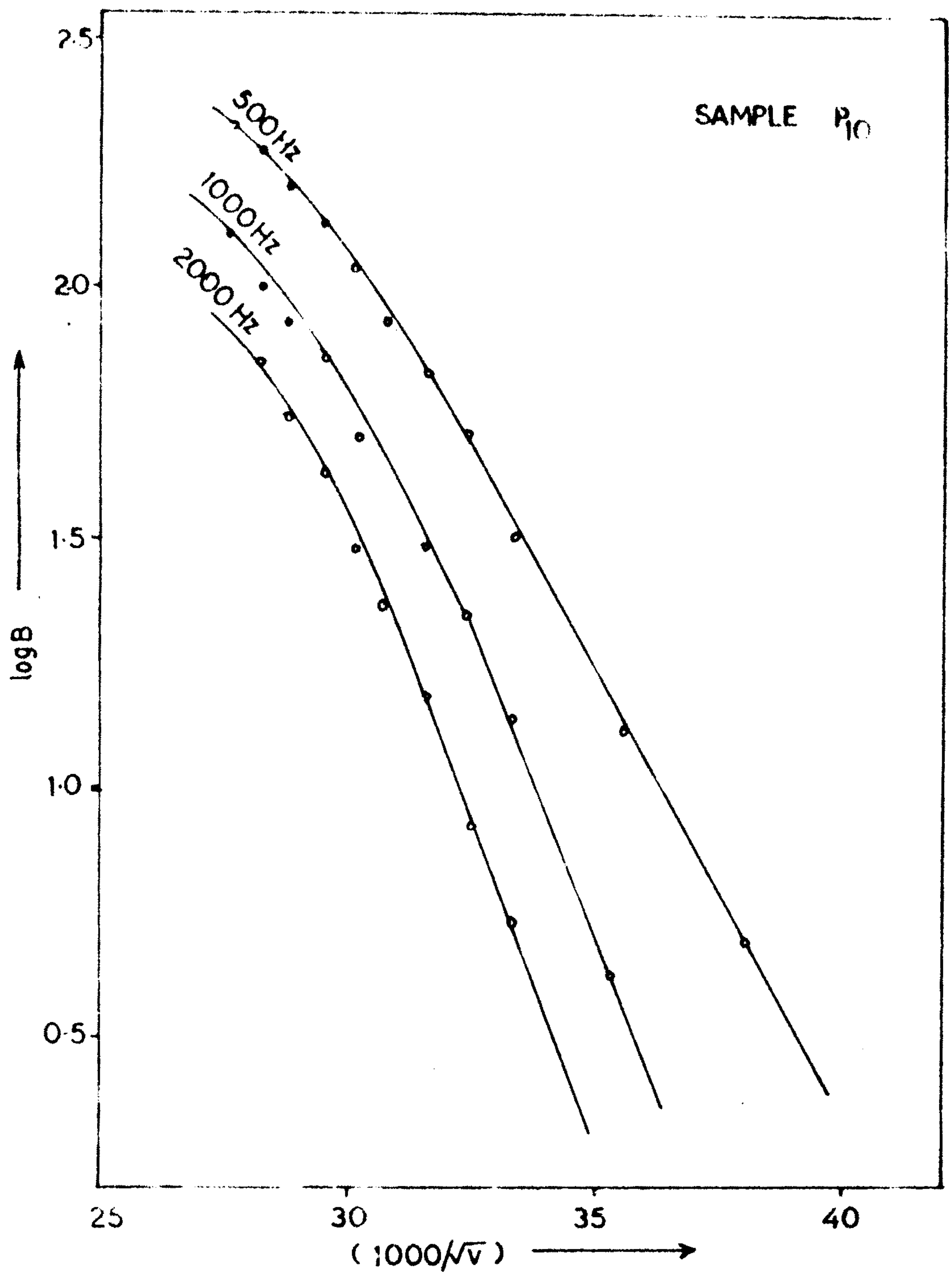

FIG. 3·7 —— PLOTS OF LOGB Vs. (1000/√v)

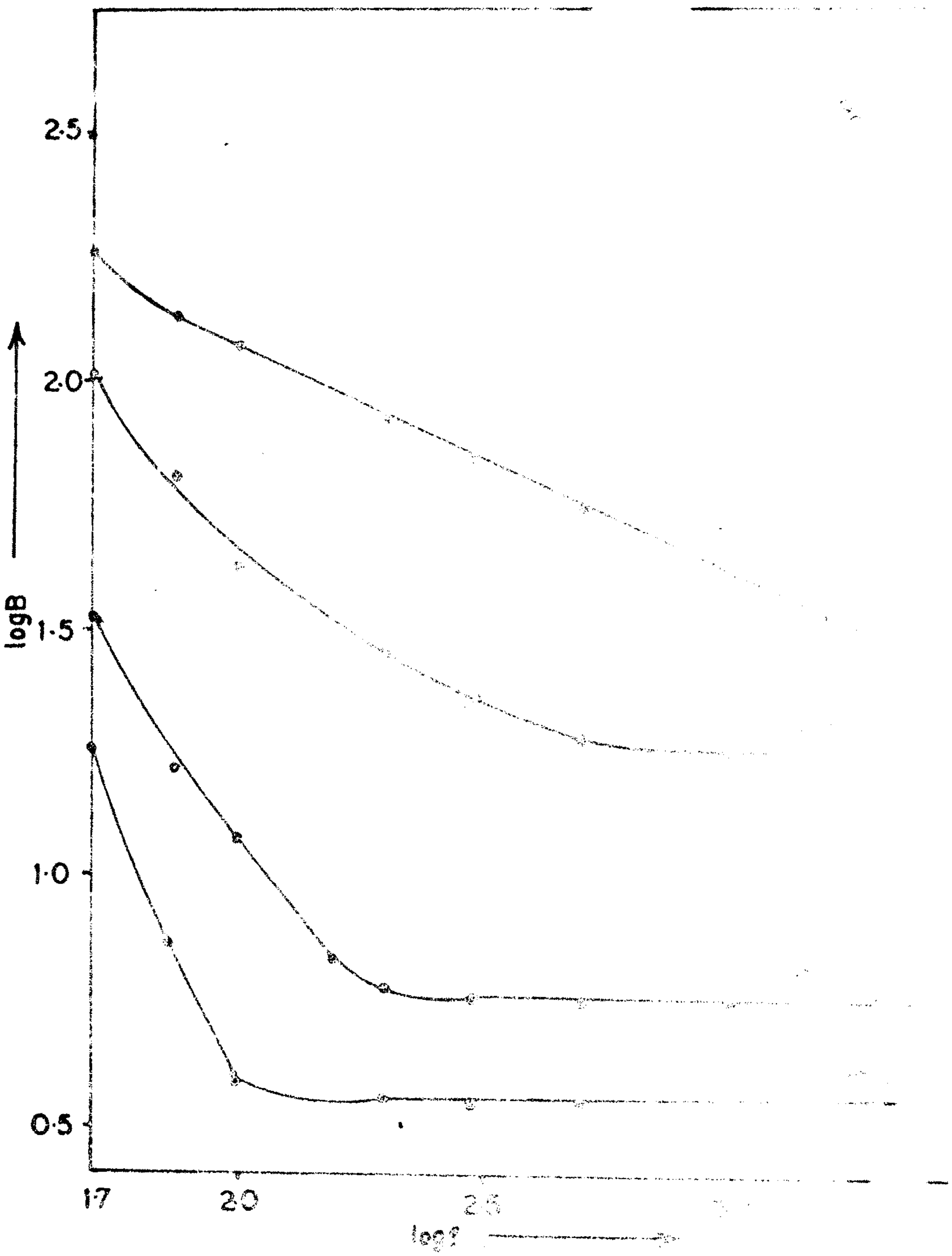

FIG. 3·8 —— PLOTS OF LOGB Vs. LOG

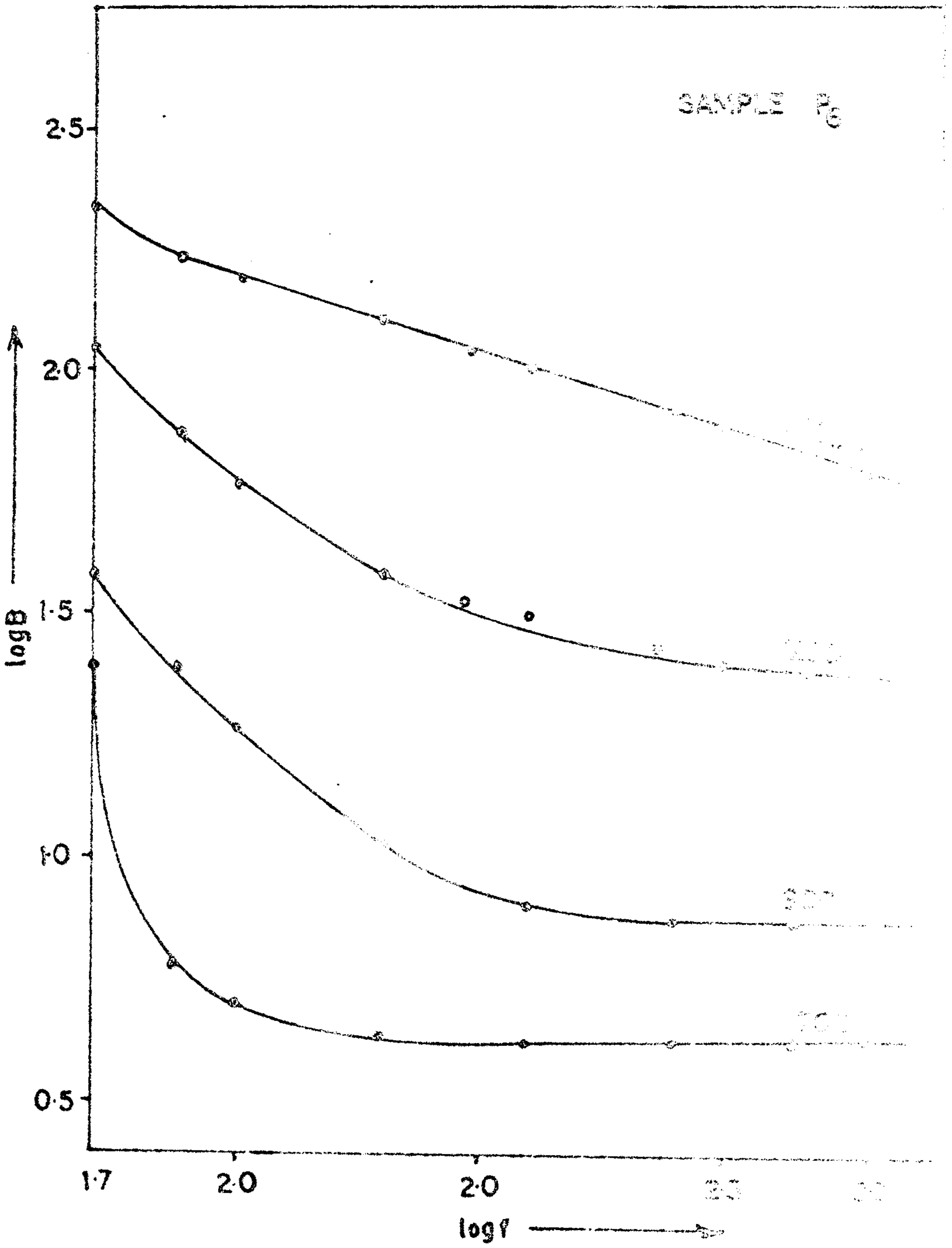

FIG. 3·9 ——PLOTS OF LOGB Vs LOGf

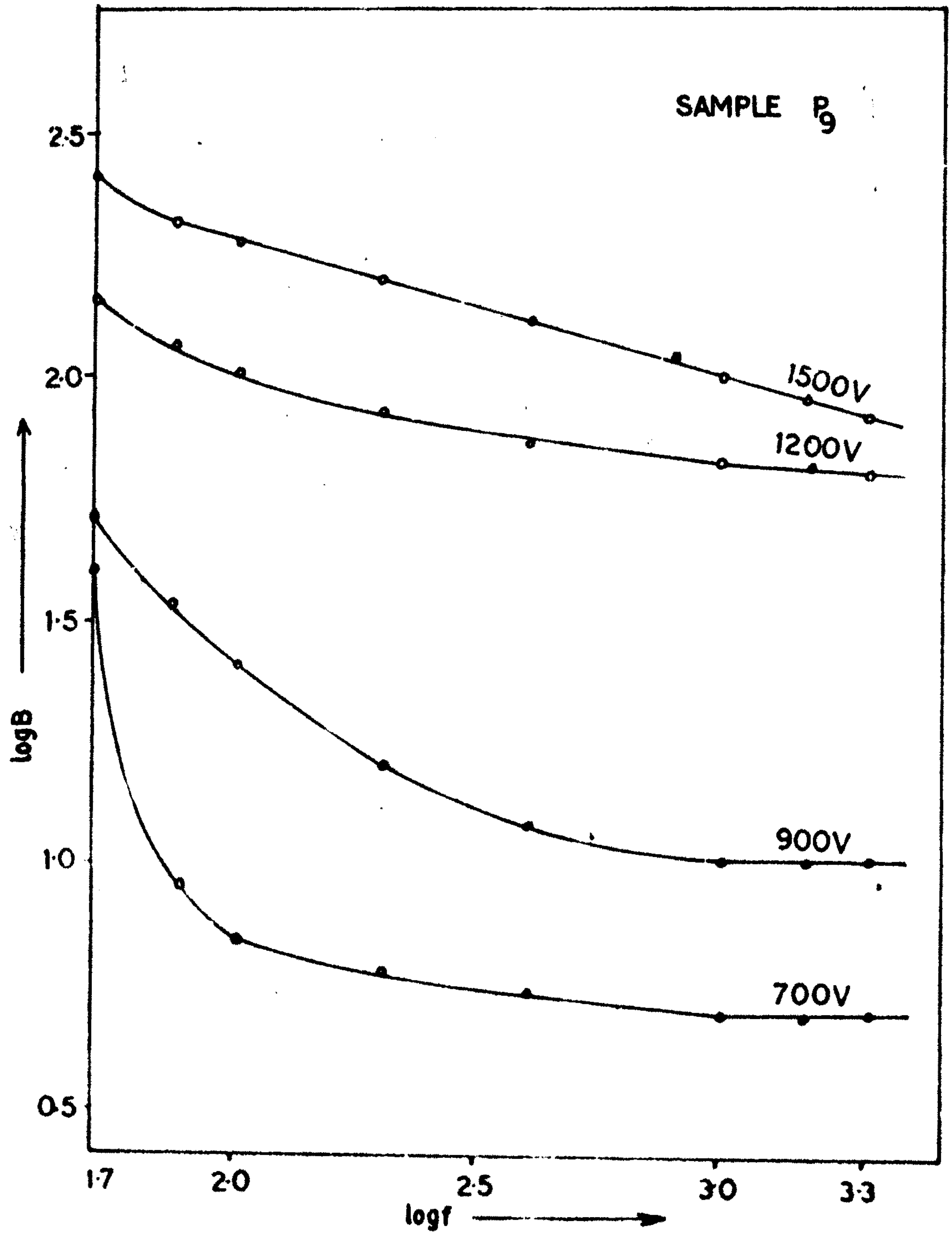

FIG. 3·10 —— PLOTS OF LOGB Vs. LOGf

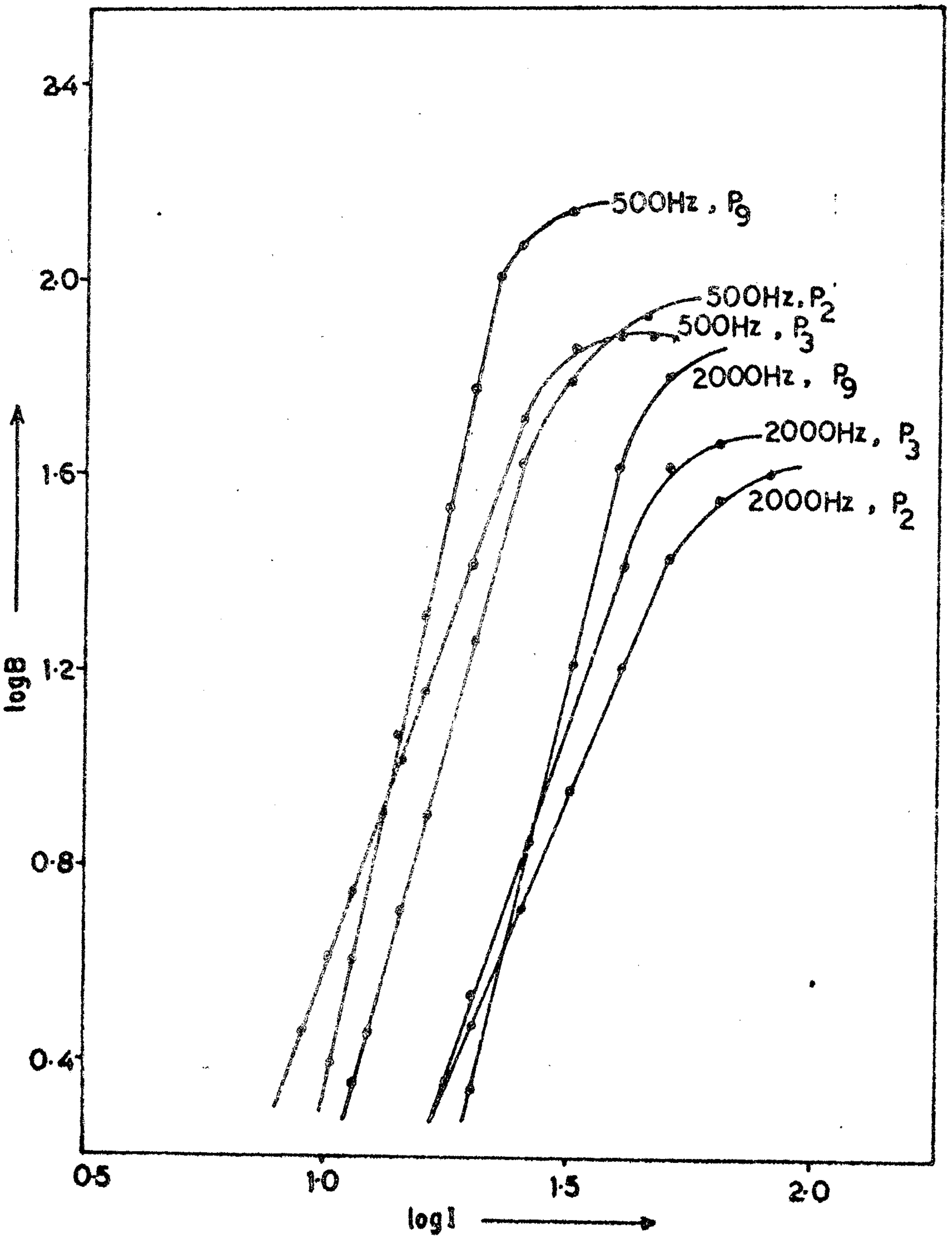

FIG. 3·11—PLOTS OF LOGB Vs. LOGI.

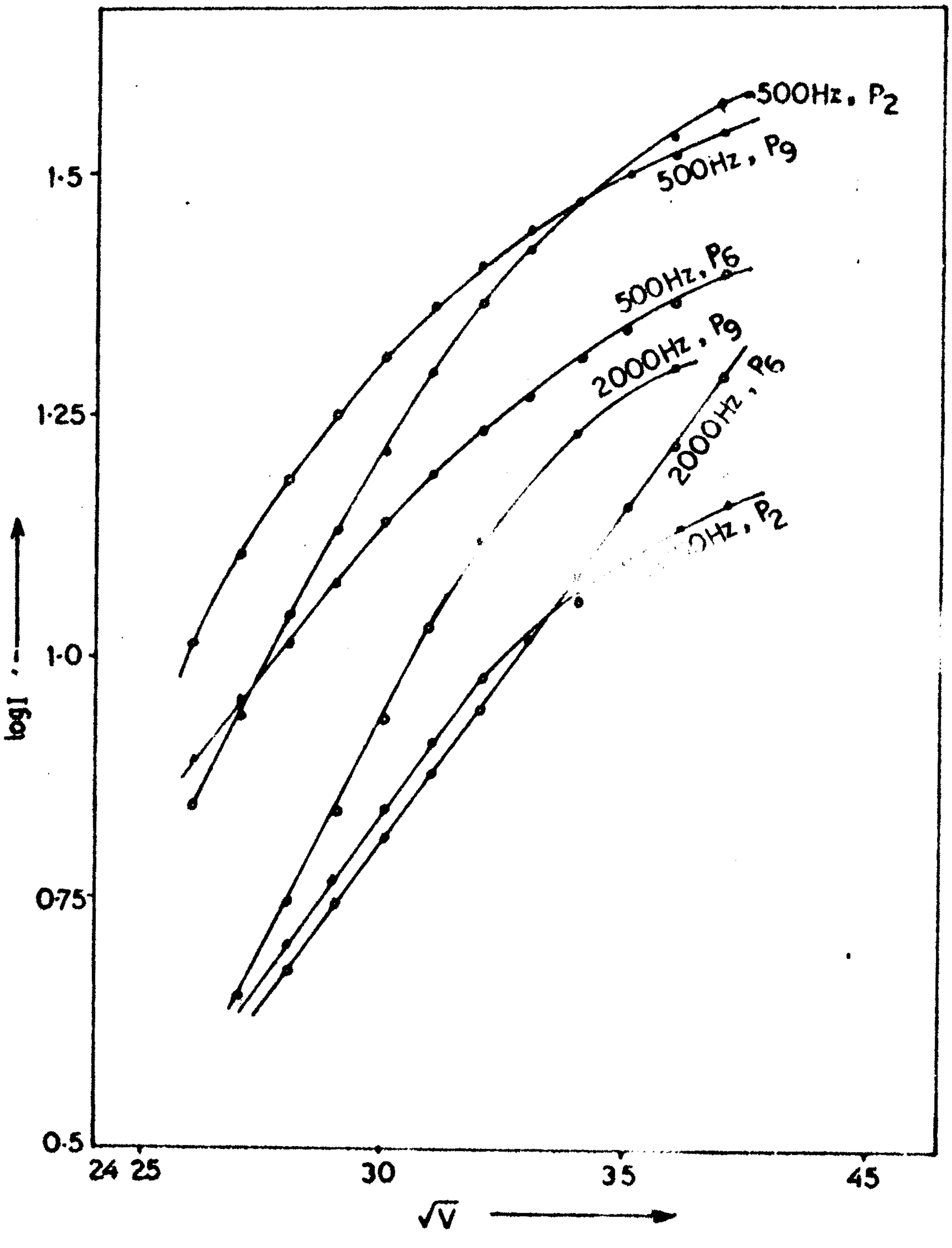

FIG. 3·12——PLOTS OF LOGI Vs √V

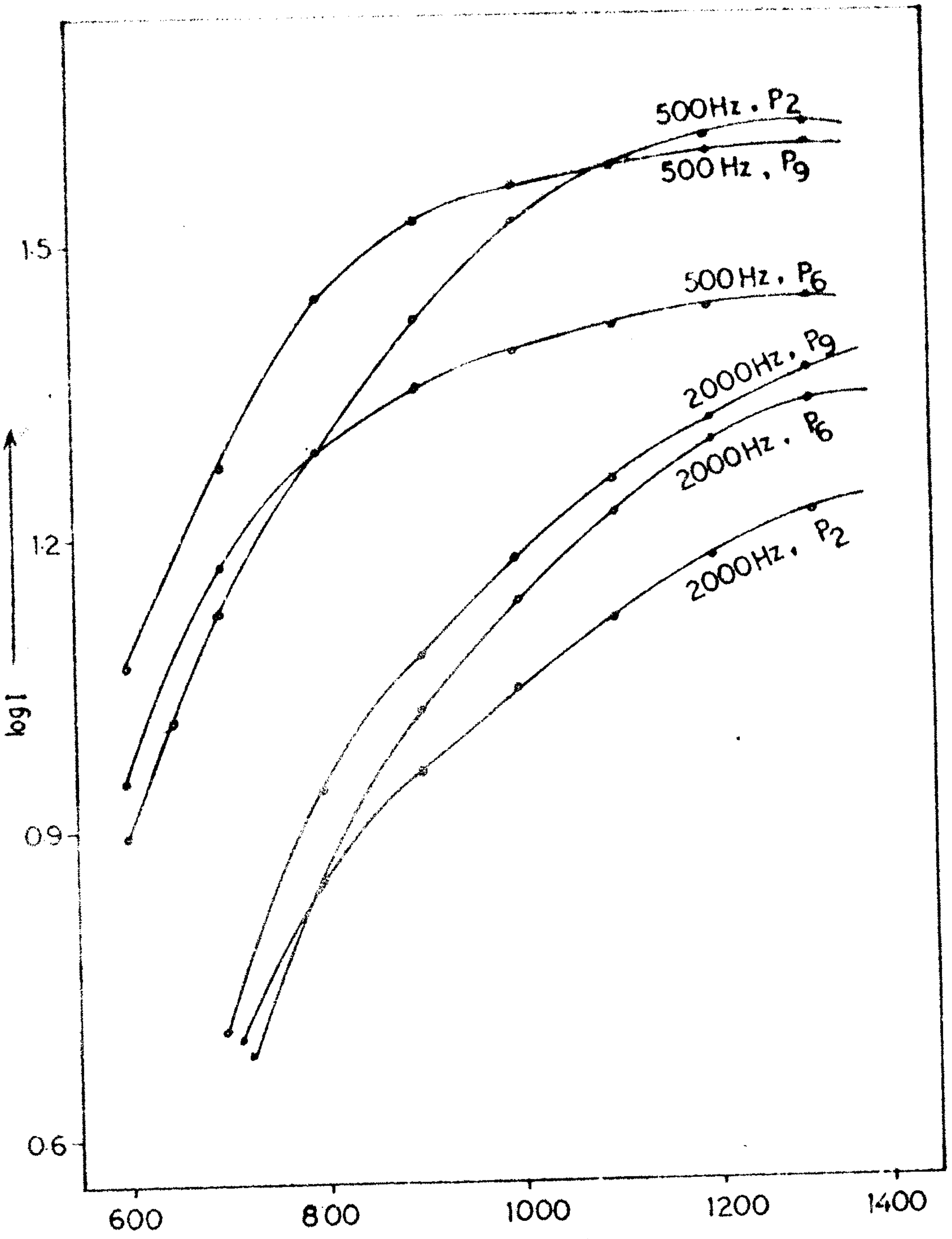

FIG. 3·13 —— PLOTS OF LOGI Vs. V.

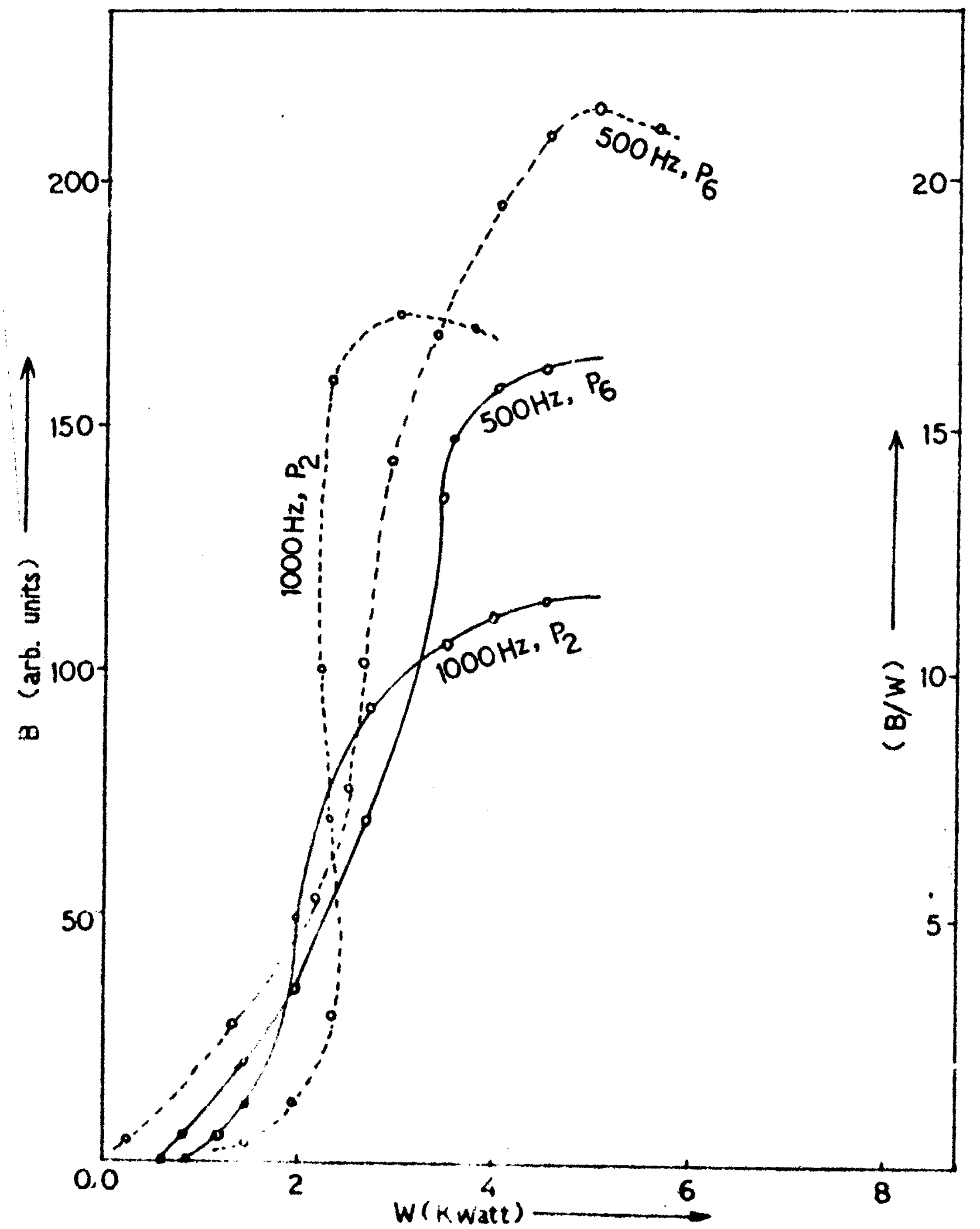

FIG 3·14 B Vs W (Full line curves)
B/W Vs W (Dotted line curves)

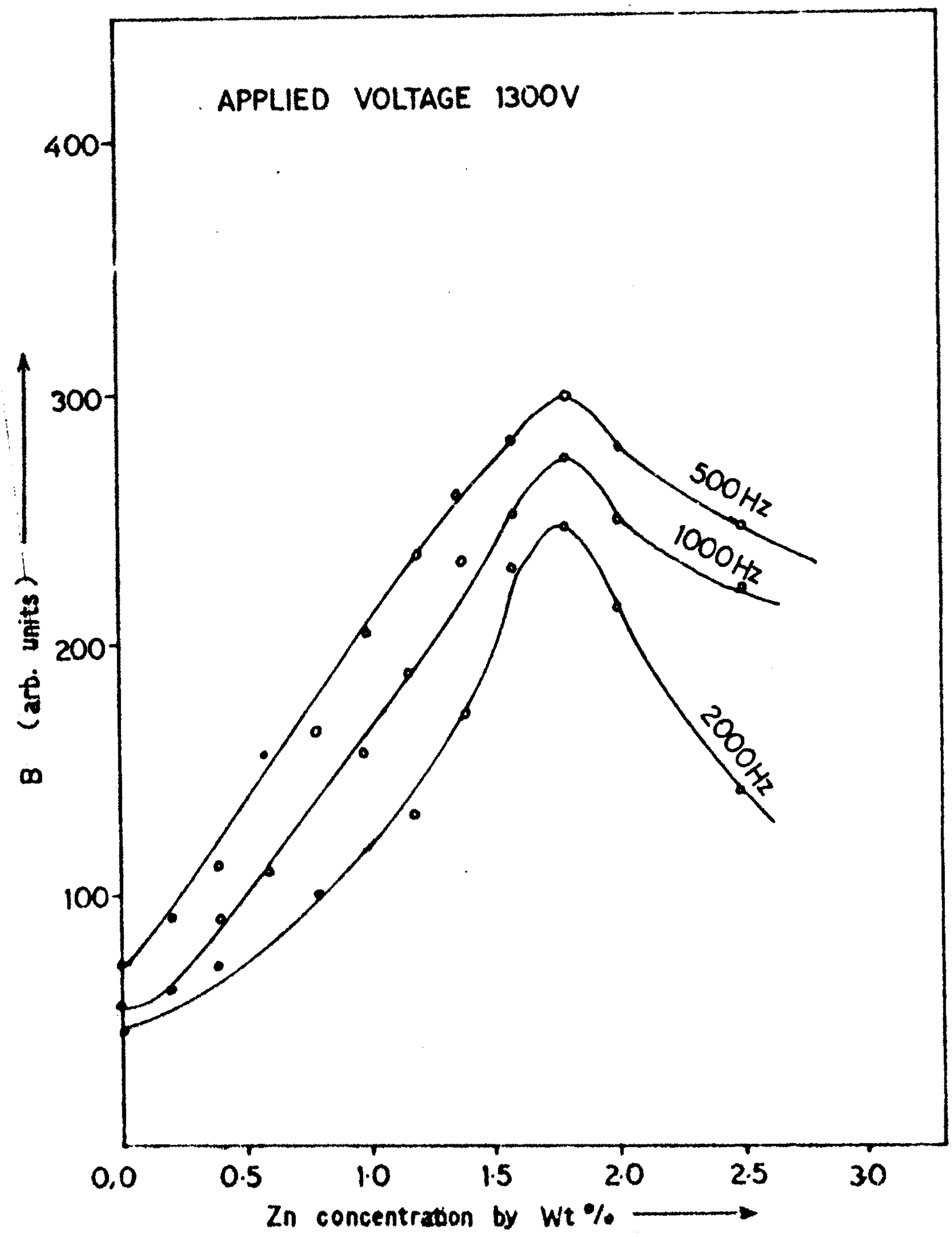

FIG. 3·16 PLOTS OF B Vs. Zn CONCENTRATION BY Wt %.

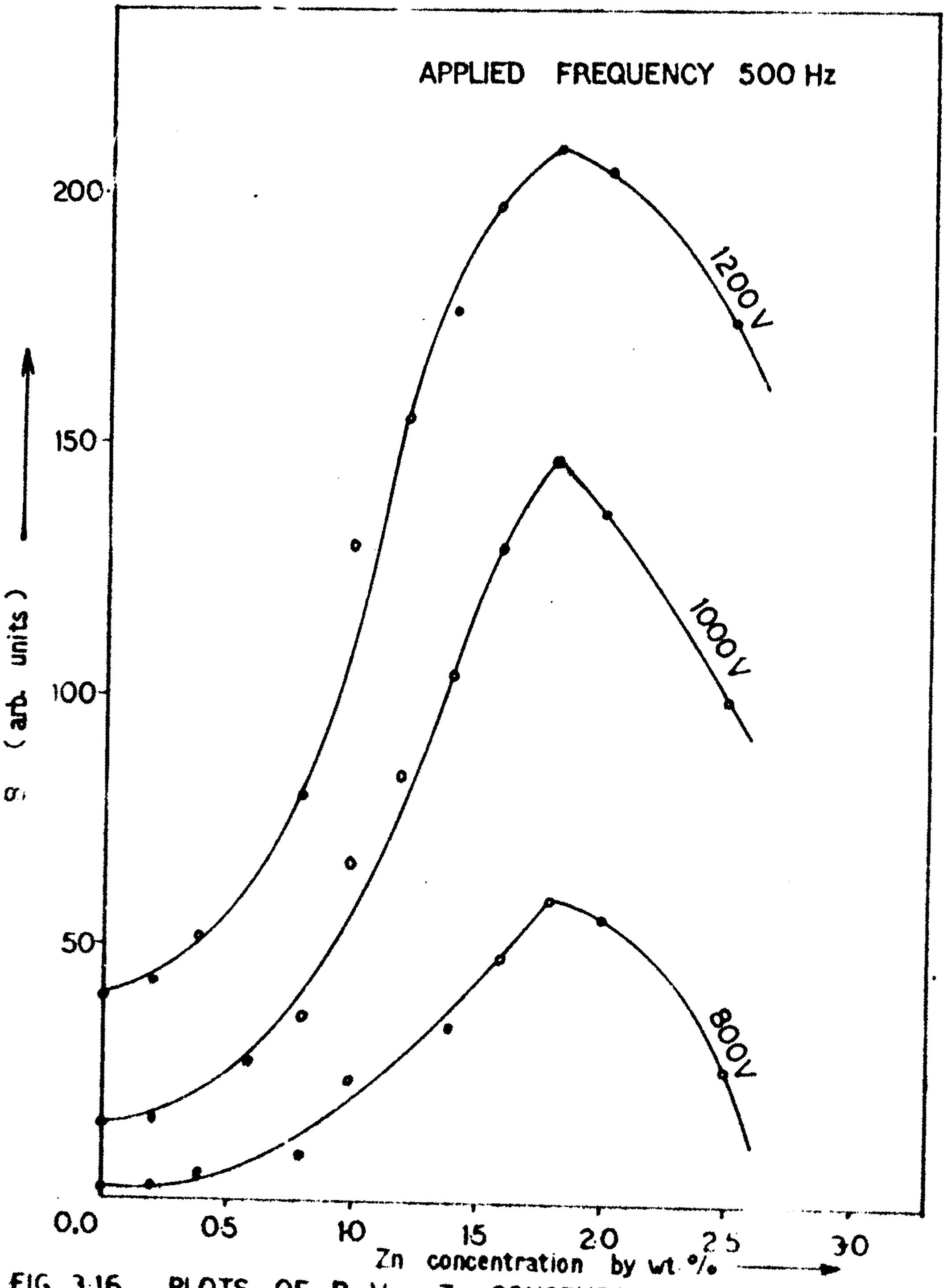

FIG. 3.16 PLOTS OF B Vs. Zn CONCENTRATION BY Wt %