STUDIES OF RADIANT HEAT TRANSFER FROM PURE GASES

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TABLE OF CONTENTS

PART	TITLE	PAGE
I	INTRODUCTION AND SUMMARY	1
II	FUNDAMENTAL RELATIONS OF RADIANT HEAT TRANSFER	3
III	ABSORPTION COEFFICIENTS A. Introduction B. Experimental Results C. Calculation of Approximate Average Absorption Coefficients	9
IV	APPROXIMATE HEAT TRANSFER CALCULATIONS FOR DIATOMIC GASES	22

ABSTRACT

This report contains an outline of some of the experimental measurements and theoretical considerations which are required for the calculation of the emissivity of nitric oxide. Because of lack of suitable apparatus, the experimental part of the program was restricted to the determination of apparent absorption coefficients for the fundamental vibration-rotation band of nitric oxide. Theoretical calculations of emissivity were originally suggested by Dr. Martin Summerfield. The present calculations were made by the use of an approximate procedure which has been developed recently at the Jet Propulsion Laboratory by S. S. Penner for the determination of the emissivity of pure diatomic gases. The results presented in this report facilitate making approximate estimates of the emissivity of nitric oxide as a function of temperature and optical density. For these emissivity calculations it is recommended to correct the experimentally determined apparent absorption coefficients by analogy with available data for carbon monoxide.

RADIANT HEAT TRANSFER FROM PURE GASES

I. INTRODUCTION AND SUMMARY

Recent development of propulsive systems and propellants capable of taxing the heat resisting properties of our best alloys has aroused considerable interest in the field of heat transfer. While this interest has led to extensive research within the broader limits of this field, the theoretical treatment of radiant heat transfer has received relatively little attention.

Theoretical studies of radiant heat transfer are based on Einstein's work on transition coefficients(1). More recent contributions from the fundamental point of view have been made by Born(2), Slater(3), and Dirac(4). As a result of this work it is now possible, in principle, to make radiant heat transfer calculations. However, the complexity of these calculations is such that they are scarcely adaptable to the numerical calculation of emissivities for practical applications.

Because of the difficulties involved in the theoretical calculations of radiant heat transfer, it has been customary to collect empirical emissivity data as a function of pressure, temperature, and path length(5). By using available emissivity data many problems on radiant heat transfer involving relatively low temperatures are now capable of approximate solution. However, since the emissivities of only a limited number of gases are known, and since, furthermore, the temperature and pressure extrapolation of available date is not possible with a high degree of accuracy, the empirical method has a rather limited range of application.

It is apparent from the foregoing considerations that a more fundamental approach to the practical problem of radiant heat transfer is highly desirable, especially for the purpose of calculating the temperature dependence of the emissivity. As the first step of a broad program on the study of radiant heat transfer now being conducted at the Jet Propulsion Laboratory, an approximate method(6) has been developed for the calculation of average emissivities of diatomic gases as a function of temperature and optical density. The present report will be devoted to the application of this method to the determination of the emissivities of nitric oxide as a function of temperature, pressure, and path length. The report is completed by a description of apparent absorption coefficient measurements of nitric oxide performed on a Model 12-C Perkin-Elmer spectrometer using a lithium-fluoride prism.

II. FUNDAMENTAL RELATIONS OF RADIANT HEAT TRANSFER

This section will be devoted to a description of some of the important basic equations of radiant heat transfer and to a discussion of the relations between line strengths, Einstein coefficients, and spectral emissivities. These equations are, of course, well known but are summarized here in order to clarify the numerical calculations of emissivities described in Section IV.

According to Beer's law for the absorption of radiation by an isotropic substance, the transmitted intensity varies exponentially according to the relation

$$I_\nu = I_{o\nu} \, e^{-P_\nu \, p \, l} \tag{1}$$

where I_ν is the intensity of the transmitted light in the spectral region between ν and $\nu + d\nu$, $I_{o\nu}$ is the intensity of the incident light in the same spectral range, P_ν is the true spectral absorption coefficient of the absorber, and the product of the pressure $\underline{p}$ and the path length $\underline{l}$ is the optical density of the absorber. The intensity of the light absorbed is, therefore,

$$A_\nu = I_{o\nu} - I_\nu = I_{o\nu} \, (1 - e^{-P_\nu \, p \, l}) \, . \tag{2}$$

According to Kirchhoff's law the ratio of the spectral emissivity to the spectral absorptivity is unity for all substances. The absorptivity is defined as the fraction of the incident light absorbed and the emissivity as the ratio of the intensity of the light emitted by a given substance at temperature T to that emitted by a blackbody at the same temperature. For an isotropic gaseous emitter, the spectral emissivity, $\mathcal{E}_\nu$, is, therefore, given by the relation

$$\mathcal{E}_\nu = 1 - e^{-P_\nu p l} \quad . \qquad (3)$$

The emissivity can be determined experimentally by direct measurement or by measuring the transmission ratios at various temperatures and pressures. Since it is difficult to make accurate measurements of this type over a wide range of temperatures and pressures, it is desirable to consider theoretically the temperature and pressure dependence of P_ν.

According to the Bohr frequency rule, transition between two nondegenerate, stationary energy states of values E_i and E_j with $E_i > E_j$ will be accompanied by the emission of radiant energy of the frequency

$$\nu_{ij} = \frac{E_i - E_j}{h} \qquad (4)$$

where h is Planck's constant.

For radiation emitted from an oscillating dipole, if the time between collisions is large compared to the duration of a collision, it can be shown(7) that the spectral absorption coefficient is related to the line strength, $\int_{-\infty}^{+\infty} P_{\nu_{ij}} d\nu_{ij}$, and the spectral-line half-width, δ_{ij}, by the well-known dispersion formula of Lorentz,

$$P_\nu = \frac{\frac{\delta_{ij}}{\pi} \int_{-\infty}^{+\infty} P_{\nu_{ij}} d\nu_{ij}}{(\nu - \nu_{ij})^2 + \delta_{ij}^2} \quad . \qquad (5)$$

The spectral-line half-width is defined as the frequency interval for which absorption is greater than one-half the maximum absorption.

Reference to equation (5) indicates that the absorption coefficient can be calculated if the line strength and the line shape are known. Although the spectral half-width is a function of temperature and pressure, this dependence will not be discussed in this report, since it is desired to present an approximate method for radiant heat transfer calculations in which no explicit allowance is made for the change of δ_{ij} with pressure and temperature. Since the line strength is independent of pressure(8), it remains only to discuss its temperature dependence in order to determine P_ν as a function of temperature. Theoretical calculations of $\int_{-\infty}^{+\infty} P_\nu \, d\nu$ as a function of temperature require the use of relations which can be derived from the Einstein coefficients of absorption and emission(9). These relations will now be discussed.

The probability that a molecule will absorb a quantum of energy and undergo a transition to a higher energy level in a blackbody radiation field is given by the term $B_{j\rightarrow i}\rho(\nu_{ij})$ where $B_{j\rightarrow i}$ is the Einstein transition coefficient of induced absorption and $\rho(\nu_{ij})$ is the density of radiation emitted by a blackbody between frequencies ν_{ij} and $\nu_{ij} + d\nu_{ij}$. The probability of transition from an upper to a lower energy level is, on the other hand, the sum of two parts, one being independent and the other proportional to the radiation density, i.e.:

$$A_{i\rightarrow j} + B_{i\rightarrow j}\rho(\nu_{ij})$$

where $B_{i\rightarrow j}$ and $A_{i\rightarrow j}$ are the Einstein coefficients of induced and spontaneous emission, respectively. At thermal equilibrium the net rate of transition is zero, and, therefore,

$$N_iA_{i\rightarrow j} = (N_jB_{j\rightarrow i} - N_iB_{i\rightarrow j})\,\rho(\nu_{ij})$$

where N_i and N_j are the number of molecules in the i'th and j'th energy levels. Noting that the net energy absorbed is

$$E_a = (N_jB_{j\rightarrow i} - N_iB_{i\rightarrow j})\,h\nu_{ij}\,\rho(\nu_{ij}) \qquad (6)$$

and defining the spectral line strength in absorption(10) by the relation

$$E_a = c\rho(\nu_{ij})\int_{-\infty}^{+\infty} P\nu_{ij}\, d\nu_{ij} \qquad (7)$$

where c is the velocity of light, it follows that

$$\int_{-\infty}^{+\infty} P\nu_{ij}\, d\nu_{ij} = N_iA_{i\rightarrow j}h\nu_{ij}/c\rho(\nu_{ij}) \qquad (8)$$

Equation (8) is the fundamental relation between line strength in absorption and the Einstein coefficient of spontaneous emission.

The net rate at which molecules jump from the upper to the lower energy level is assumed to be given by an expression of the form(10)

$$N_i\left[A_{i\rightarrow j} + B_{i\rightarrow j}\,\rho'(\nu_{ij})\right] - N_jB_{j\rightarrow i}\,\rho'(\nu_{ij}) \qquad (9)$$

where $\rho'(\nu_{ij})$ is the external radiation density. Hence for $\rho'(\nu_{ij})$ vanishingly small the emitted radiant intensity is

$$\int_{-\infty}^{+\infty} I\nu_{ij}\, d\nu_{ij} = N_iA_{i\rightarrow j}\,h\nu_{ij} \qquad (10)$$

which defines the line strength in emission $\int_{-\infty}^{+\infty} I_{\nu_{ij}} d\nu_{ij}$, for an $i \rightarrow j$ transition. From equations (8) and (10) it can be seen that

$$\int_{-\infty}^{+\infty} I_{\nu_{ij}} d\nu_{ij} = c\rho(\nu_{ij}) \int_{-\infty}^{+\infty} P_{\nu_{ij}} d\nu_{ij} \qquad (11)$$

which is equivalent to Kirchhoff's law.

For a transition between the adjacent vibrational levels n-1 and n the line strength in absorption is given, approximately, by the following relation

$$\int_{n-1\rightarrow n} P_\nu \, d\nu = \frac{h\nu_0}{c\rho(\nu_0)} N_n A_{n\rightarrow n-1} \qquad (12)$$

where

$$\int_{n-1\rightarrow n} P_\nu \, d\nu = \sum_j \left\{ \int_{\substack{n-1\rightarrow n\\ j\rightarrow j-1}} P_\nu \, d\nu + \int_{\substack{n-1\rightarrow n\\ j-1\rightarrow j}} P_\nu \, d\nu + \int_{\substack{n-1\rightarrow n\\ j\rightarrow j}} P_\nu \, d\nu \right\}^{*}, \qquad (13)$$

and

$$A_{n\rightarrow n-1} = \sum_j \left\{ A_{\substack{n\rightarrow n-1\\ j\rightarrow j-1}} + A_{\substack{n\rightarrow n-1\\ j-1\rightarrow j}} + A_{\substack{n\rightarrow n-1\\ j\rightarrow j}} \right\} . \qquad (14)$$

Equation (12) involves the approximation of replacing the different frequencies corresponding to different vibration-rotation transitions by an average value, ν_0, which, as a good approximation, may be set equal to the frequency difference corresponding to the vibrational transition $n = 0 \rightarrow n = 1$ and the rotational transition $j = 0 \rightarrow j = 0$.

The use of Planck's law of radiation, of Boltzmann's equation for the population of molecules in different vibrational levels under

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*It should be noted that NO has a permanent electric moment in the direction of the internuclear axis, and that, therefore, its infrared vibration-rotation spectrum shows P, Q, and R branches.

equilibrium conditions, and of Bohr's correspondence principle permits the derivation of the following relation$^{(6, 11, 12)}$

$$\int_{n-1\rightarrow n} P_\nu \, d\nu \approx \frac{N_T \pi \mathcal{E}^2}{3\mu c} \left\{1 - e^{-\frac{h\nu_o}{kT}}\right\} \frac{n\, e^{-(n-1)\frac{h\nu_o}{kT}}}{\sum_{n=1}^{\infty} e^{-(n-1)\, h\nu_o/kT}}$$

or

$$\sum_{n=0}^{\infty} \int_{n-1\rightarrow n} P_\nu \, d\nu \approx \frac{N_T \pi \mathcal{E}^2}{3\, \mu\, c} \qquad (15)$$

where N_T is the total number of molecules, $\mathcal{E}$ is the effective charge, and μ is the reduced mass of the molecule. Equation (15) states that the summation of the line strengths contributing to emission or absorption in the region of the fundamental vibration-rotation band is independent of the temperature for a given number of emitters. This relation will be used in the approximate calculation of emissivities described in Section IV.

III. ABSORPTION COEFFICIENTS

A. INTRODUCTION

This section is devoted to a discussion of true, apparent, and average absorption coefficients. The introduction includes a brief description of the methods used by Bourgin(13) and Bartholomé(14) for the determination of true absorption coefficients. Because of lack of suitable equipment for the determination of the true absorption coefficients, the experimental studies were restricted to the measurement of apparent absorption coefficients. The significance, use, and temperature dependence of an apparent average absorption coefficient will also be considered.

The method used by Bourgin does not permit the determination of true absorption coefficients directly, but does allow the calculation of spectral line-strengths. Once spectral line-strengths have been obtained it is possible to calculate true absorption coefficients by application of the Lorentz dispersion formula (Cf. Eq. 5) provided half-width data have also been obtained. The general plan used by Bourgin for determining line intensities involves the accurate measurement of the area under each absorption line for several cell lengths, the pressure being maintained constant.* Because the instrument available for the present experiment did not give sufficiently high resolution, Bourgin's method could not be used. If a plot is made of percentage of light absorbed against wave number, it follows that the area A_M, under the absorption line M is given by the expression

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*It is evident that this technique requires high spectral resolution in order to separate the rotational fine structure of the absorption band.

$$A_M = \int_M \left[1 - \frac{I_\nu}{I_{o\nu}}\right] d\nu \qquad (16)$$

Expanding the exponential term in Beer's law for sufficiently small values of the optical density, pl, leads to the relation

$$\frac{I_\nu}{I_{o\nu}} \approx 1 - P_\nu \, pl \qquad (17)$$

Combining equations (16) and (17) yields the result that

$$A_M = pl \int_M P_\nu \, d\nu \qquad (18)$$

From equation (18) it then follows that

$$\lim_{pl \to 0} \frac{d A_M}{dpl} = \int_M P_\nu \, d\nu \qquad (19)$$

i.e., the integrated absorption coefficient, or the line strength, is equal to the slope of an area versus length plot for the limiting case of zero cell length. In order to permit accurate extrapolation of this curve to zero, small cell lengths were employed. It should be mentioned that the extrapolation of the curve to the zero value of the optical density becomes a difficult problem because of the rapid change of slope of the curve at small values of pl.

Bartholomé's method has the advantage over Bourgin's of not requiring high resolution. By the introduction in the light absorption cell of another gas which is optically inactive in the infrared region of study, the total pressure is increased to the point where the rotational lines overlap sufficiently to obliterate completely the fine structure. This method is now being employed at the Jet Propulsion Laboratory to determine the relation between the true absorption coefficient and an absorption coefficient measured with low resolution and at low pressures, i.e., an apparent absorption coefficient.

Before proceeding to discuss the apparent absorption coefficient, it is of interest to note that an approximate method is available for the determination of an average value of the line strength for a given absorption band. This method was originally proposed by Dennison(15) and has been modified by Cornell(16), Elsasser(17), Summerfield(18), and others. The principal objection to this method is the necessity for assuming that the rotational lines are of equal intensity and are equally spaced. In spite of the fact that these assumptions are invalid for real molecules, it should be pointed out that the method of Elsasser and Summerfield has been shown to lead to reasonable numerical results(17, 18).

B. EXPERIMENTAL RESULTS

The apparent absorption coefficient, $P_\nu^!$, is a coefficient replacing the true absorption coefficient, P_ν, in Beer's law and is determined with resolution insufficient to study individual rotational lines and at pressures lower than required to give complete overlapping of the rotational lines. Since the necessary facilities for carrying out an accurate determination of the true line strength were not available at the time the studies described in this thesis were conducted, it was decided to measure apparent absorption coefficients with the infrared spectrometer available to the author. It is recognized that the relation between true and apparent coefficients is unknown. However, the preliminary measurements of apparent coefficients described in this thesis should be of value ultimately to the overall program of heat transfer now under way at the Jet Propulsion Laboratory. By use of the empirically determined relations between true and apparent coefficients for CO, the values of the apparent coefficients of NO can be converted approximately to the true values. That the true and apparent absorption coefficients for CO and NO should be related follows from the similarity in rotational spacing and resolution in the P and R branches of the fundamental absorption bands of these two compounds. The apparent absorption coefficients were determined by straightforward application of Beer's law. From the linearized form of this law, it can be seen that

$$\ln \frac{I_\nu}{I_{o\nu}} = - P_\nu' \, pl \tag{20}$$

where P_ν' is, in general, a function of pressure. In the limiting case of zero optical density, pl, it can be seen that

$$P_\nu' = - \lim_{pl \to 0} d\left[\ln (I_\nu/I_{o\nu})\right] / d(pl) \tag{21}$$

Since the path length was kept constant because cells of different lengths were not available, equation (21) may be written as

$$P_\nu' = - \frac{1}{l} \lim_{p \to 0} d\left[\ln (I_\nu/I_{o\nu})\right] / dp \tag{22}$$

from which it follows that the apparent absorption coefficient is proportional to the limiting slope, for zero pressure, of a plot of the logarithm of the fraction of the light transmitted as a function of pressure. In the present investigations the pressure of the absorber was kept below 1 atmosphere in order to permit more accurate extrapolation of the curve to zero pressure. Readings were made at pressures of NO corresponding to 13.5, 15.9, 28.3, 36.5, 48.0, 71.6, and 72.0 cm. of Hg.

All measurements were made on a Model 12C, Perkin-Elmer infrared spectrometer using a lithium fluoride prism and a 10 cm. long gas cell closed with sodium chloride windows. A resolution of about 4 wave numbers was obtained near the center of Q-branch for the fundamental vibration-rotation band of NO with the particular slit widths employed for the present studies. The wave length scale had been previously calibrated by using known absorption lines of H_2O, CO_2, CH_4, and NH_3. A wave length-micrometer scale reading calibration curve obtained by the author is shown in figure (1).

Prior to taking transmission readings on the infrared spectrometer, the instrument was allowed the customary warm-up period of one-half hour in order to insure stable operation. Next a transmission record was obtained for the empty gas cell. Then a transmission record was obtained for the cell filled with the gas under the study, and finally another reference run with the evacuated cell was completed. From these three sets of data it is possible to obtain reasonably reliable percentage of transmission values as a function of wave length. The wave length calibration curve was checked daily by using the water bands at 1794, 1830, 1846, 1870, 1891, and 1944 cm^{-1} as reference points. The wave length calibration led to a value for the wave number at the peak of the Q-branch of 1877.9 cm^{-1} which agrees reasonably well with results reported by other investigators(19, 20, 21).

Representative data of the logarithm of the percentage of transmission as a function of pressure, calculated from the experimental measurements are shown in figures (2) and (3). The values of the apparent absorption coefficient computed from these plots are summarized in Table I and are plotted in figure (4) as a function of the wave number.

TABLE I

APPARENT ABSORPTION COEFFICIENTS FOR NO.

ν cm^{-1}	P_{ν}' $(meter\text{-}atm)^{-1}$
1800.0	1.38
1816.5	3.05
1850.8	6.33
1866.4	7.11
1877.9	11.28
1881.8	2.58
1896.8	7.05
1907.7	9.00
1917.0	9.20
1924.0	8.58
1936.1	6.85
1954.0	2.00

C. CALCULATION OF APPROXIMATE AVERAGE ABSORPTION COEFFICIENTS.

From the discussion in Section II it is apparent that rigorous calculation of spectral emissivities at various temperatures is a project of tremendous proportions. In order to avoid some of the difficulties of radiant heat transfer calculations it was proposed by Schack(22) to use an absorption coefficient which is a linear function of the wave number for a given absorption band. Schack used available experimental measurements for the apparent absorption coefficient, a procedure which is certainly not justified.

The procedure of Schack for making emissivity calculations can be further simplified if average absorption coefficients for entire absorption bands are used. It is clear that if, as a first approximation, it is possible to use such average coefficients, then the average coefficients are defined in terms of the effective emissivity by the relation

$$\mathcal{E}' = (1 - e^{-\bar{k}_F\, pl})\frac{\int_{\lambda_{min}}^{\lambda_{max}} I_\lambda\, d\lambda}{\int_0^{+\infty} I_{o\nu}\, d\nu} + (1 - e^{-\bar{k}_{F.O.}\, pl})\frac{\int_{\lambda'_{min}}^{\lambda'_{max}} I_\lambda\, d\lambda}{\int_0^{+\infty} I_{o\lambda}\, d\lambda} + \cdots \quad (23)$$

where $\mathcal{E}'$ - effective emissivity
$\bar{k}_F$ - average absorption coefficient for the fundamental band
$\bar{k}_{F.O.}$ - average absorption coefficient for the first overtone
$_{max}$ - long wave length cut-off for fundamental
$_{min}$ - short wave length cut-off for fundamental
$_{max}$ - long wave length cut-off for first overtone
$_{min}$ - short wave length cut-off for first overtone

The effective band width of the fundamental is $\lambda_{max} - \lambda_{min}$, and for the first overtone it is $\lambda'_{max} - \lambda'_{min}$. The effective band width may be looked upon as the wave length interval over which absorption is of consequence according to a prearranged standard. By comparison of equation (23) with the following relation, which can be derived from equation (2),

$$\sum_n \sum_j \int_{\substack{n\to n+1\\ j\to j-1}} E_\nu \, d\nu + \sum_n \sum_j \int_{\substack{n\to n+1\\ j-1\to j}} E_\nu \, d\nu + \sum_n \sum_j \int_{\substack{n\to n+1\\ j\to j}} E_\nu \, d\nu =$$

$$c \sum_n \sum_j \int_{\substack{n\to n+1\\ j\to j-1}} \rho(\nu) \, (1 - e^{-P_\nu pl}) \, d\nu + c \sum_n \sum_j \int_{\substack{n\to n+1\\ j-1\to j}} \rho(\nu) (1 - e^{-P_\nu pl}) \, d\nu +$$

$$c \sum_n \sum_j \int_{\substack{n\to n+1\\ j\to j}} \rho(\nu) \, (1 - e^{-P_\nu pl}) \, d\nu \qquad (24)$$

it can be shown (6) that the average coefficients, if they exist, are of the form

$$\bar{k}_F = \frac{1}{\Delta\nu_F} \sum_n \sum_j \left\{ \int_{\substack{n\to n+1\\ j-1\to j}} P_\nu \, d\nu + \int_{\substack{n\to n+1\\ j\to j-1}} P_\nu \, d\nu + \int_{\substack{n\to n+1\\ j\to j}} P_\nu \, d\nu \right\} \qquad (25)$$

$$\bar{k}_{F.O.} = \frac{1}{\Delta\nu_{F.O.}} \sum_n \sum_j \left\{ \int_{\substack{n\to n+2\\ j\to j-1}} P_\nu \, d\nu + \int_{\substack{n\to n+2\\ j-1\to j}} P_\nu \, d\nu + \int_{\substack{n\to n+2\\ j\to j}} P_\nu \, d\nu \right\} \qquad (26)$$

Here, $\int\limits_{\substack{n\rightarrow n+1\\ j\rightarrow j-1}} E_\nu \, d\nu$ represents, for example, the intensity of radiation absorbed as the result of the transition $n\rightarrow n+1$, $j\rightarrow j-1$, and $\Delta\nu_F$ and $\Delta\nu_{F.O.}$ are the effective band widths of the fundamental and first overtone, respectively.

Relations of the form of equations (25) and (25a) permit the calculation of average absorption coefficients if the sum of the true line strengths is known. As has been pointed out previously, the present experiments yielded only apparent absorption coefficients. Nevertheless, it is instructive to consider the relations between apparent spectral absorption coefficients and apparent average absorption coefficients. In order to distinguish apparent average coefficients from the true average coefficients, the former will be designated by $\overline{k}'_F$, $\overline{k'}_{F.O.}$, etc. The experimentally observed result that for small values of the optical density, the average apparent absorption coefficient, defined by the relation

$$\int\limits_{\Delta\nu_F} A_\nu \, d\nu = \left\{1 - e^{-\overline{k}'_F pl}\right\} \int\limits_{\Delta\nu_F} I_{o\nu} \, d\nu \tag{26}$$

is identical with the average apparent absorption coefficient

$$\overline{k}'_F = \frac{\int\limits_{\Delta\nu_F} P_\nu' d\nu}{\Delta\nu_F} \tag{27}$$

will now be established on the basis of a more detailed analysis of equation (26).

In the limiting case of small pl, the exponential term in equation (26) can be expanded and only the first two terms retained with the result

$$\int_{\Delta\nu_F} A_\nu \, d\nu \Big/ \int_{\Delta\nu_F} I_{o\nu} \, d\nu = \bar{k}'_F \, pl \tag{28}$$

from which it follows that for constant path length, l,

$$\frac{1}{l} \frac{d}{dp} \left\{ \frac{\displaystyle\int_{\Delta\nu_F} A_\nu \, d\nu}{\displaystyle\int_{\Delta\nu_F} I_{o\nu} \, d\nu} \right\} = \bar{k}'_F \tag{29}$$

Furthermore, integration of the spectral form of Beer's Law for the apparent coefficient, P_ν', and for small values of $P_\nu' \, p \, l$,

$$\left(1 - \frac{I_\nu}{I_{o\nu}}\right) = P_\nu' \, p \, l, \tag{30}$$

yields the result that

$$\int_{\Delta\nu_F} \frac{(I_{o\nu} - I_\nu) \, d\nu}{I_{o\nu}} = pl \int_{\Delta\nu_F} P_\nu' \, d\nu \tag{31}$$

If the energy of the incident light is nearly independent of frequency within the limits of the effective band width, then equation (31) can be replaced, approximately, by the relation

$$\frac{\int_{\Delta\nu_F}(I_{o\nu} - I_\nu)\,d\nu}{\int_{\Delta\nu_F} I_{o\nu}\,d\nu} = \frac{\int_{\Delta\nu_F} A_\nu\,d\nu}{\int_{\Delta\nu_F} I_{o\nu}\,d\nu} = \frac{pl}{\Delta\nu_F}\int_{\Delta\nu_F} P'_\nu\,d\nu$$

and, therefore,

$$\frac{1}{l}\,\frac{d}{dp}\left\{\frac{\int_{\Delta\nu_F} A_\nu\,d\nu}{\int_{\Delta\nu_F} I_{o\nu}\,d\nu}\right\} = \frac{\int_{\Delta\nu_F} P'_\nu\,d\nu}{\Delta\nu_F} \qquad (32)$$

Comparison of equations (29) and (32) leads to the desired result

$$\bar{k}'_F = \frac{\int_{\Delta\nu_F} P'_\nu\,d\nu}{\Delta\nu_F} \quad . \qquad (27)$$

It should be noted that equation (27) between the apparent average absorption coefficient and the apparent spectral coefficient is of the same form as equations (25) and (25a) relating the true average coefficients to the spectral line strengths.

Empirical proof of the existence of an average apparent absorption coefficient can be obtained by comparison of the values of $\bar{k}'_F$ calculated by means of equations (27) and (29), respectively. Data for equation (27) was obtained by numerical integration of figure (4), which resulted in a value for the $\int_{\Delta\nu_F} P'_\nu\,d\nu$ of 965.2 (meter-atm-cm)$^{-1}$. The effective band width was chosen as 198 cm^{-1}. Substitution of these values in equation (27) yielded a value of $\overline{k}_F' = 5.03$ $(meter\text{-}atm)^{-1}$ for the average apparent absorption coefficient. For evaluation of the average coefficient by means of equation (29), suitable band limits were chosen by inspection of the transmission records for the various pressures, and the areas under the transmission lines between these limits were obtained by numerical integration. The ratios of the integrated percentage of absorption were then plotted as functions of pressure in figure (5) and the slope of the line noted. Substitution in equation (29) gave a value of 4.78 $(meter\text{-}atm)^{-1}$ for $\overline{k}_F'$. The approximate equality of the two values for $\overline{k}_F'$ may be taken as proof of the existence of an average apparent absorption coefficient.

The average apparent absorption coefficient is related to the true average absorption coefficient, which can be expressed in terms of the sum of the individual line strengths according to equation (25), in a complicated fashion depending upon instrumental resolution. However, since the rotational spacing and resolution for studies of the apparent absorption coefficients of CO(6) and NO were similar, it is reasonable to assume that the true average absorption coefficient bears the same relation to the apparent average absorption coefficient for these two gases. This ratio has been found to be 23 for CO*. It is therefore recommended, that an average absorption coefficient $\overline{k}_F$ 23×5.03 $(meter \times atm)^{-1} = 115.69$ $(meter \times atm)^{-1}$ be used for radiant heat transfer calculations on NO until more reliable experimental measurements become available.

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*Unpublished results obtained by S. S. Penner and D. Weber

The temperature dependence of $\bar{k}_F$ can be calculated by use of equations (15) and (25). Reference to these two relations indicates that

$$\frac{\bar{k}_F(T_2)}{\bar{k}_F(T_1)} = \frac{\Delta\nu_F(T_1)}{\Delta\nu_F(T_2)} \cdot \frac{T_1}{T_2} \qquad (33)$$

since the number of molecules per unit volume, N_T, varies inversely as the absolute temperature for an ideal gas.

IV. APPROXIMATE RADIANT HEAT TRANSFER CALCULATIONS FOR DIATOMIC GASES

This section contains an outline of the method(6) developed at the **Jet Propulsion** Laboratory for making approximate radiant heat transfer calculations for diatomic gases with specific application to nitric oxide. The existence and the value of the average absorption coefficient having been dealt with at length in Section III, it is assumed that this coefficient exists and is known for the fundamental vibration-rotation band as a function of temperature. Equation (23)

$$\varepsilon' = (1 - e^{-\bar{k}_F pl}) \frac{\int_{\lambda_{min}}^{\lambda_{max}} I_\lambda \, d\lambda}{\int_0^{+\infty} I_{o\lambda} \, d\lambda} + (1 - e^{-\bar{k}_{F.O.} pl}) \frac{\int_{\lambda'_{min}}^{\lambda'_{max}} I_\lambda \, d\lambda}{\int_0^{+\infty} I_{o\lambda} \, d\lambda} + \dots \quad (23)$$

will be used to calculate the effective emissivity.

Examination of equation (23) indicates that the calculation of emissivities requires the determination of the band limits. Although pressure has the effect of broadening the individual lines, the individual line strength remaining constant, it is obvious that pressure will have practically no effect on the effective band width. This conclusion follows since broadening a line whose strength is negligibly small cannot have an appreciable effect on the band width. It is possible, however, in the case of extremely high pressures, to have a line of significant strength boradened sufficiently to cause a measurable widening of the band. The present method of calculation is, therefore, not suitable for pressures greater than a few hundred atmospheres.

Before proceeding a description of the physical appearance of the absorption band of NO and a statement of the relation between the component parts of the band and particular transitions are of interest. The band is composed of three distinct branches designated as the P, Q, and R branches, respectively. The P-branch is the high frequency branch, the R-branch is the low frequency branch, and the Q-branch forms the center of the band and joins the P- and R-branches. The rotational transitions $j-1 \rightarrow j$ are responsible for the R-branch, the transitions $j \rightarrow j-1$ for the P-branch, and the transitions $j \rightarrow j$ for the Q-branch. The number of rotational transitions associated with line strengths large enough to contribute appreciably to radiation from the P- and R-branches is the same, as can be shown by a detailed analysis of the dependence of line strength on rotational quantum number.(6)

It is well known that a factor of the type $j \exp(-E_{o,j}/kT)$ or $j \exp(-E_{o,j}/kT)$ is the dominant term depending on j in the expression for line strength. Use can be made of this fact, if as a first approximation, the band limits are chosen as those points at which the strengths of the individual rotational lines tend to zero. The criterion used for the proper choice of j_{max} was arbitrarily chosen as that value of j for which $j \exp(-E_{o,j}/kT)$ corresponds approximately to 10^{-3} of the maximum value of $j \exp(-E_{o,j}/kT)$. A study of figures (6) through (11) in which $j \exp(-E_{o,j}/kT)$ has been plotted as a function of j at 300, 1000, 1500, 2000, 2500, 3000° K indicates that no very great difference in j_{max} results if the value of j_{max} is set equal to the value of j for which j exp $(-E_{o,j}/kT)$ has decreased to 10^{-2} or 10^{-4} of its maximum value. It should be noted that the emissivity does not depend critically on the value of j_{max} because the uncertainty in the value of j_{max} is partly compensated for by a larger or smaller average absorption coefficient if too small or too large a value has been chosen, respectively, for j_{max}. Band emissivity calculations have been carried out for values of j_{max} corresponding to somewhat different criteria for choosing j_{max}. By the use of figures (6) through (11) the values of j_{max_1} and j_{max_2} given in Table II were obtained for calculating the probable effective band widths where j_{max_1} corresponds to the value of j for which j exp $(-E_{o,j}/kT)$ has decreased to approximately 10^{-3} of its maximum value.

TABLE II

THE VALUES OF j_{max_1} and j_{max_2} AS A FUNCTION OF TEMPERATURE

T	j_{max_1}	j_{max_2}
300	30	33
1000	54	58
1500	65	69
2000	77	81
2500	88	91
3000	100	106

By use of the familiar quantum relation the approximate band limits of the fundamental can, therefore, be determined as follows:

$$\nu_{\substack{\max \\ n\rightarrow n-1 \\ j\rightarrow j-1}} = \frac{E(n,\ j_{max}) - E(n-1,\ j_{max} - 1)}{h\ c} \qquad (34)$$

$$\nu_{\substack{\min \\ n\rightarrow n-1 \\ j-1\rightarrow j}} = \frac{E(n, j_{max} - 1) - E(n-1, j_{max})}{h\ c} \qquad (34a)$$

The energy levels of NO can be calculated from following relation

$$\frac{E\ (n,j)}{hc} = (n+\tfrac{1}{2})\omega_e - (n+\tfrac{1}{2})\ x_e\omega_e + j\ (j+1)\ B_e - j^2(j+1)^2D_e - (n+\tfrac{1}{2})j(j+1)\alpha \qquad (35)$$

where ω_e, B_e, D_e, x_e, and α are well-known constants for NO determined from spectroscopic measurements. The following numerical values were used for NO: $\omega_e = 1906.5\ cm^{-1}$; $x_e = 0.7564 \times 10^{-2}$; $B_e = 1.7006\ cm^{-1}$ $D_e = 5.4124\ cm^{-1}$; $\alpha = 1.8366 \times 10^{-2} cm^{-1}$ (23). The spectroscopic data for NO has recently been revised by Gillette and Eyster(21). However, for the present purposes, the data given by Sponer are sufficiently accurate. The approximate band limits of the fundamental of NO as calculated from equations (34) and (34a) are tabulated below as functions of temperature for the values of j_{max_1};

TABLE III

APPROXIMATE BAND LIMITS FOR THE FUNDAMENTAL OF NO

T	j_{max_1}	ν_{max}, cm^{-1}	ν_{min}, cm^{-1}	$\Delta\nu$, cm^{-1}	λ_{max} cm	λ_{min} cm
300	30	1961.5	1760.9	200.6	5.6789	5.0981
1000	54	2002.7	1645.8	356.9	6.0761	4.9932
1500	65	2012.8	1587.4	425.4	6.2996	4.9682
2000	77	2018.3	1519.4	498.9	6.5815	4.9547
2500	88	2016.8	1454.0	562.8	6.8776	4.9583
3000	100	2009.3	1379.4	629.9	7.2495	4.9768

A study of Table II indicates that as T, and therefore j_{max} increases, λ_{min} passes through a minimum (bandhead) somewhere between 1500 and 2500°K and thereafter increases with temperature. It can be seen that since λ_{min} is a double-valued function of j the effect of choosing a j_{max} value larger than that corresponding to the bandhead has the effect of eliminating a number of transitions which contribute materially to radiant heat transfer. Therefore, in order to avoid this difficulty the value of j corresponding to the bandhead should be used for those temperatures where the calculated value of j_{max} is larger than the j value corresponding to the bandhead(6). The value of j_{max} corresponding to the bandhead was accurately determined as $j_{max} = 80$ by noting the energy maximum of the $j \rightarrow j-1$ transitions. Tables IV and V contain the band limits for the fundamental band of NO for j_{max_1} and j_{max_2}, with proper allowance for the existence of the bandhead.

TABLE IV

BAND LIMITS OF FUNDAMENTAL OF NITRIC OXIDE

CALCULATED FROM THE VALUE OF j_{max_1}

T	j_{max_1}	ν_{max}, cm^{-1}	ν_{min}, cm^{-1}	$\Delta\nu$, cm^{-1}	λ_{max}, cm	λ_{min}, cm
300	30	1961.5	1760.9	200.6	5.6789	5.0981
1000	54	2002.7	1645.8	356.9	6.0761	4.9932
1500	65	2012.8	1587.4	425.4	6.2996	4.9682
2000	77	2018.3	1519.4	498.9	6.5815	4.9547
2500	80-88	2018.8	1454.0	564.8	6.8776	4.9534
3000	80-100	2018.8	1379.4	639.4	7.2495	4.9534

TABLE V

BAND LIMITS OF FUNDAMENTAL OF NITRIC OXIDE

CALCULATED FROM THE VALUES OF j_{max_2}

T	j_{max_2}	ν_{max}, cm^{-1}	ν_{min}, cm^{-1}	$\Delta\nu$, cm^{-1}	λ_{max}, cm	λ_{min}, cm
300	33	1968.0	1747.5	220.5	5.7225	5.0813
1000	58	2007.2	1625.1	382.1	6.1535	4.9821
1500	69	2015.3	1565.7	449.6	6.3869	4.9620
2000	80-81	2018.8	1496.2	522.6	6.6866	4.9534
2500	80-91	2018.8	1435.8	583.0	6.9648	4.9534
3000	80-106	2018.8	1340.7	678.1	7.4588	4.9534

Detailed examination of the line strength(6) indicates that the overtone will decrease to 10^{-3} of its maximum value at approximately the same value of j_{max} as the fundamental. The same j_{max} values have, therefore, been used for the first overtone as for the fundamental. Tables V and VI summarize the band limits for the first overtone of NO corrected for the bandhead for the two choices of j_{max}. The bandhead in the case of the first overtone, determined by the same detailed calculations as for the fundamental, occurred at $j_{max} = 44$.

TABLE VI

BAND LIMITS OF FIRST OVERTONE OF NITRIC OXIDE

CALCULATED FROM THE VALUES OF j_{max_1}

T	j_{max_1}	ν'_{max}, cm^{-1}	ν'_{min}, cm^{-1}	$\Delta\nu'$cm^{-1}	λ'_{max}, cm	λ'_{min}, cm
300	30	3793.4	3593.9	199.5	2.7825	2.6362
1000	44-54	3800.7	3442.1	358.6	2.9052	2.6311
1500	44-65	3800.7	3360.0	440.7	2.9762	2.6311
2000	44-77	3800.7	3260.3	540.4	3.0672	2.6311
2500	44-88	3800.7	3162.2	638.5	3.1624	2.6311
3000	44-100	3800.7	3045.9	754.8	3.2831	2.6311

TABLE VII

BAND LIMITS OF FIRST OVERTONE OF NITRIC OXIDE CALCULATED FROM THE VALUES OF j_{max_2}

T	j_{max_2}	ν_{max}, cm^{-1}	ν_{min}, cm^{-1}	$\Delta\nu$, cm^{-1}	λ_{max}, cm	λ_{min}, cm
300	33	3796.0	3577.0	219.0	2.7956	2.6344
1000	44-58	3800.7	3412.0	388.7	2.9300	2.6311
1500	44-69	3800.7	3328.3	472.4	3.0045	2.6311
2000	44-81	3800.7	3226.1	574.6	3.0997	2.6311
2500	44-91	3800.7	3134.0	666.7	3.1908	2.6311
3000	44-106	3800.7	2985.0	815.7	3.3350	2.6311

In figures (12) and (13) the effective band limits are shown as a function of temperature for the NO fundamental and first overtone of NO, respectively.

The band limits having been found, the intensity ratios, $\int_{\Delta\nu} I_\nu \, d\nu / \int_0^{+\infty} I_{0\nu} \, d\nu$, in equation (23) can readily be evaluated by the use of Planck's radiation functions. An abbreviated table of these functions is shown in Table VIII. The intensity ratios have been plotted for the fundamental and first overtone of NO as functions of temperature in figure (14). It should be noted that these ratios represent the maximum attainable values of the contributions to the total emissivity for a given vibration-rotation band, and that, therefore, their sum represents the total maximum emissivity. Figure (14) indicates that the peak emissivity for the fundamental occurs at approximately 850° K and for the first overtone at 1500° K. These results can be understood qualitatively in terms of the temperature dependence of the wave length at which the intensity of radiation is a maximum (Wien's displacement law).

The average absorption coefficient for the fundamental can be calculated at different temperatures by means of equation (33). Similar calculations can be made to determine the average absorption coefficient for the first overtone as a function of temperature if the room temperature value of $\bar{k}_{F.O.}$ is known. If the room temperature value of $\bar{k}_F$ has not been determined experimentally, then it can be calculated, approximately, by an equation given by Rosenthal$^{(24)}$,

$$\frac{\bar{k}_{F.O.}}{\bar{k}_F} \simeq \frac{x_e(1-5x_e)}{(1-3x_e)^2} \qquad (36)$$

where x_e is the anharmonicity constant which has a value of 0.756×10^{-2} for NO. Using equation (36) and the value for the fundamental average absorption coefficient of 115.69 (meter-atm)$^{-1}$, the value of first overtone average coefficient at room temperature is found to be 88.09×10^{-2} (meter-atm)$^{-1}$.

The necessary information is now available to calculate the emissivity of NO as a function of temperature. Because of the uncertainties in the numerical value of $\bar{k}_F$ discussed in section III, emissivity tables have not been calculated for NO. However, in order to facilitate the use of the results described in this thesis for making approximate emissivity calculations, the procedure for determining the emissivity of NO as a function of temperature is outlined again in some detail.

The Calculation of the Emissivity of NO

The emissivity of NO is given by the approximate relation

$$\mathcal{E}' = (1 - e^{-\bar{k}_F pl}) \frac{\int_{\lambda\,min}^{\lambda\,max} I_\lambda \, d\lambda}{\int_0^{+\infty} I_{o\lambda} d\lambda} + (1 - e^{-\bar{k}_{F.O.} pl}) \frac{\int_{\lambda'min}^{\lambda'max} I_\lambda d\lambda}{\int_0^{+\infty} I_{o\lambda} d\lambda} + \cdots \qquad (23)$$

The ratios $\int_{\lambda min}^{\lambda max} I_\lambda d\lambda \Big/ \int_0^{+\infty} I_{o\lambda} d\lambda$ and $\int_{\lambda' min}^{\lambda' max} I_\lambda d\lambda \Big/ \int_0^{+\infty} I_{o\lambda} d\lambda$

are plotted in figure (14) as functions of temperature. The value of $\bar{k}_F$ can be calculated as a function of temperature from the relation

$$\bar{k}_F(T_2) = \frac{\Delta\nu_F(T_1)}{\Delta\nu_F(T_2)} \cdot \frac{T_1}{T_2} \; \bar{k}_F(T_1)$$

similarly,

$$\bar{k}_{F.O.}(T_2) = \frac{\Delta\nu_{F.O.}(T_1)}{\Delta\nu_{F.O.}(T_2)} \cdot \frac{T_1}{T_2} \cdot \bar{k}_{F.O.}(T_1)$$

The effective band widths $\Delta\nu_F$ and $\Delta\nu_{F.O.}$ are given, as a function of temperature, in tables VI and VII. The recommended values for the average absorption coefficients at 300° K are

$$\bar{k}_F = 115.69 \text{ (m x atm)}^{-1}$$

$$\bar{k}_{F.O.} = 88.09 \times 10^{-2} \text{ (m x atm)}^{-1}$$

The values of $\bar{k}_F$ and $\bar{k}_{F.O.}$ are not known accurately at the present time and may require revision as the result of current experimental studies.

If the values of the average absorption coefficients are changed, the method of calculating $\mathcal{E}'$ remains unaltered except for the use of the new values of $\overline{k}_F$ and $\overline{k}_{F.O.}$

TABLE VIII

PLANCK'S RADIATION FUNCTIONS

$$\frac{R_{0-\lambda}}{R_{0-\infty}} = F \times 10^{-p}$$

λT IN CM K°	F	p
0.050	1.3652	9
.051	2.2642	9
.052	3.6788	9
.053	5.8629	9
.054	9.1749	9
.055	1.4113	8
.056	2.1358	8
.057	3.1829	8
.058	4.6745	8
.059	6.7710	8
.060	9.6798	8
.061	1.3667	7
.062	1.9069	7
.063	2.6307	7
.064	3.5907	7
.065	4.8510	7
.066	6.4902	7
.067	8.6028	7
.068	1.1302	6
.069	1.4723	6
.070	1.9025	6
.071	2.4393	6
.072	3.1045	6
.073	3.9230	6
.074	4.9236	6
.075	6.1392	6
.076	7.6070	6
.077	9.3692	6
.078	1.1473	5
.079	1.3971	5
.080	1.6923	5
.081	2.0393	5
.082	2.4453	5
.083	2.9183	5
.084	3.4668	5
.085	4.1002	5
.086	4.8287	5
.087	5.6633	5

$$\frac{R_{0-\lambda}}{R_{0-\infty}} = F \times 10^{-p}$$

λT IN CM K°	F	p
0.090	8.9269	5
.091	1.0314	4
.092	1.1874	4
.093	1.3626	4
.094	1.5586	4
.095	1.7772	4
.096	2.0204	4
.097	2.2901	4
.098	2.5885	4
.099	2.9179	4
.100	3.2804	4
0.100	3.2804	4
.105	5.6770	4
.110	9.2957	4
.115	1.4510	3
.120	2.1727	3
.125	3.1370	3
.130	4.3866	3
.135	5.9631	3
.140	7.9053	3
.145	1.0248	2
.150	1.3023	2
.155	1.6254	2
.160	1.9962	2
.165	2.4161	2
.170	2.8858	2
.175	3.4056	2
.180	3.9754	2
.185	4.5944	2
.190	5.2613	2
.195	5.9749	2
.200	6.7331	2
.205	7.5339	2
.210	8.3750	2
.215	9.2538	2
.220	1.0168	1
.225	1.1114	1
.230	1.2091	1

TABLE VIII

PLANCK'S RADIATION FUNCTIONS (Cont'd)

$$\frac{R_{0} - \lambda}{R_{0} - oo} = F \text{ X } 10^{-p}$$

λT IN CM K°	F	p
.088	6.6159	5
.089	7.6993	5
0.250	1.6239	1
.255	1.7324	1
.260	1.8423	1
.265	1.9533	1
.270	2.0653	1
.275	2.1780	1
.280	2.2911	1
.285	2.4047	1
.290	2.5183	1
.295	2.6320	1
.300	2.7454	1
.305	2.8585	1
.310	2.9712	1
.315	3.0833	1
.320	3.1947	1
.325	3.3053	1
.330	3.4150	1
.335	3.5237	1
.340	3.6314	1
.345	3.7379	1
.350	3.8432	1
.355	3.9474	1
.360	4.0502	1
.365	4.1517	1
.370	4.2518	1
.375	4.3506	1
.380	4.4479	1
.385	4.5438	1
.390	4.6332	1
.395	4.7312	1
.400	4.8227	1
.400	4.8327	1
.410	5.0012	1
.420	5.1738	1
.430	5.3404	1
.440	5.5012	1

$$\frac{R_{0} - \lambda}{R_{0} - oo} = F \text{ X } 10^{-p}$$

λT IN CM K°	F	p
.235	1.3094	1
.240	1.4122	1
.245	1.5171	1
0.500	6.3494	1
.510	6.4727	1
.520	6.5912	1
.530	6.7051	1
.540	6.8146	
.550	6.9198	1
.560	7.0209	1
.570	7.1182	1
.580	7.2116	1
.590	7.3014	1
.600	7.3877	1
.600	7.3877	1
.620	7.5505	1
.640	7.7010	1
.660	7.8402	1
.680	7.9691	1
.700	8.0885	1
.720	8.1993	1
.740	8.3020	1
.760	8.3974	1
.780	8.4861	1
.800	8.5687	1
.820	8.6455	1
.840	8.7172	1
.860	8.7840	1
.880	8.8465	1
.900	8.9048	1
.920	8.9494	1
.940	9.0105	1
.960	9.0584	1
.980	9.1033	1
1.000	9.1455	1
1.00	9.1455	1
1.05	9.2402	1
1.10	9.3217	1
1.15	9.3921	1
1.20	9.4532	1

TABLE VIII

PLANCK'S RADIATION FUNCTIONS (Cont'd)

$$\frac{R_{0-\lambda}}{R_{0-\infty}} = F \times 10^{-p}$$

λT IN CM K°	F	p
.450	5.6563	1
.460	5.8057	1
.470	5.9495	1
.480	6.0880	
.490	6.2212	1

$$\frac{R_{0-\lambda}}{R_{0-\infty}} = F \times 10^{-p}$$

λT IN CM K°	F	p
1.25	9.5065	1
1.30	9.5531	1
1.35	9.5942	1
1.40	9.6304	1
1.45	9.6624	1
1.50	9.6909	1
1.55	9.7163	1
1.60	9.7390	1
1.65	9.7594	1
1.70	9.7777	1
1.75	9.7942	1
1.80	9.8091	1
1.85	9.8226	1
1.90	9.8349	1
1.95	9.8461	1
2.00	9.8563	1

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TABLE OF SYMBOLS

A_{ν} - intensity of light absorbed
$A_{i \rightarrow j}$ - Einstein coefficient of spontaneous emission
A_M - area under rotational line
$B_{i \rightarrow j}$ - Einstein coefficient of induced emission
$B_{j \rightarrow i}$ - Einstein coefficient of induced absorption
c - velocity of light
E - energy
h - Planck's constant
i - upper energy level
I_{ν} - intensity of transmitted light
$I_{o\nu}$ - intensity of incident light
j - lower energy level; rotational quantum number
k - Boltzmann's constant
$\bar{k}_F$ - True average absorption coefficient for fundamental
$\bar{k}_{F.O.}$ - True average absorption coefficient for first overtone
$\bar{k}'_F$ - Apparent average absorption coefficient for fundamental
$\bar{k}'_{F.O.}$ - Apparent average absorption coefficient for first overtone
l - path length
N - molecular population
n - vibrational quantum number
p - pressure
pl - optical density
P_{ν} - True spectral absorption coefficient
P_{ν}' - Apparent absorption coefficient
T - Absolute temperature

GREEK SYMBOLS

δ - Spectral half-width

ε - effective charge

ε' - effective emissivity

ε_ν - spectral emissivity

λ - wave length

μ - reduced mass; microns

ν - wave number, frequency

ν_0 - frequency corresponding to $n = 0 \rightarrow n = 1$; $j = 0 \rightarrow j = 0$

$\rho(\nu)$ - density of radiation of blackbody

$\rho'(\nu)$ - external density of radiation

$\int P_\nu d\nu$ - line strength in absorption

UNITS

$A_{i\to j}$ - $(\mathrm{cc\ x\ sec})^{-1}$

$B_{i\to j}$; $B_{j\to i}$ - $(\mathrm{erg\ x\ sec\ x\ sec})^{-1}$

P_{ν} - $(\mathrm{meter\ x\ atm})^{-1}$

$\int P_{\nu}\, d\nu$ - $(\mathrm{meter\ x\ atm\ x\ cm})^{-1}$

$\int I_{\nu}\, d\nu$ - ergs/cc x sec

$\rho(\nu)$ - erg x sec/cc

ν - cm^{-1}

λ - cm, microns

LIST OF FIGURES

1- Wave Length Calibration Curve for Perkin-Elmer Mod. 12C Spectrometer with Lithium Fluoride Prism.

2- Logarithm of Percentage of Transmission as a Function of Pressure for NO at 1850.8 cm^{-1}.

3- Logarithm of Percentage of Transmission as a Function of Pressure for NO at 1936.1 cm^{-1}.

4- Apparent Absorption Coefficient of NO as a Function of Wave Number (Resolution $\approx 4\ cm^{-1}$).

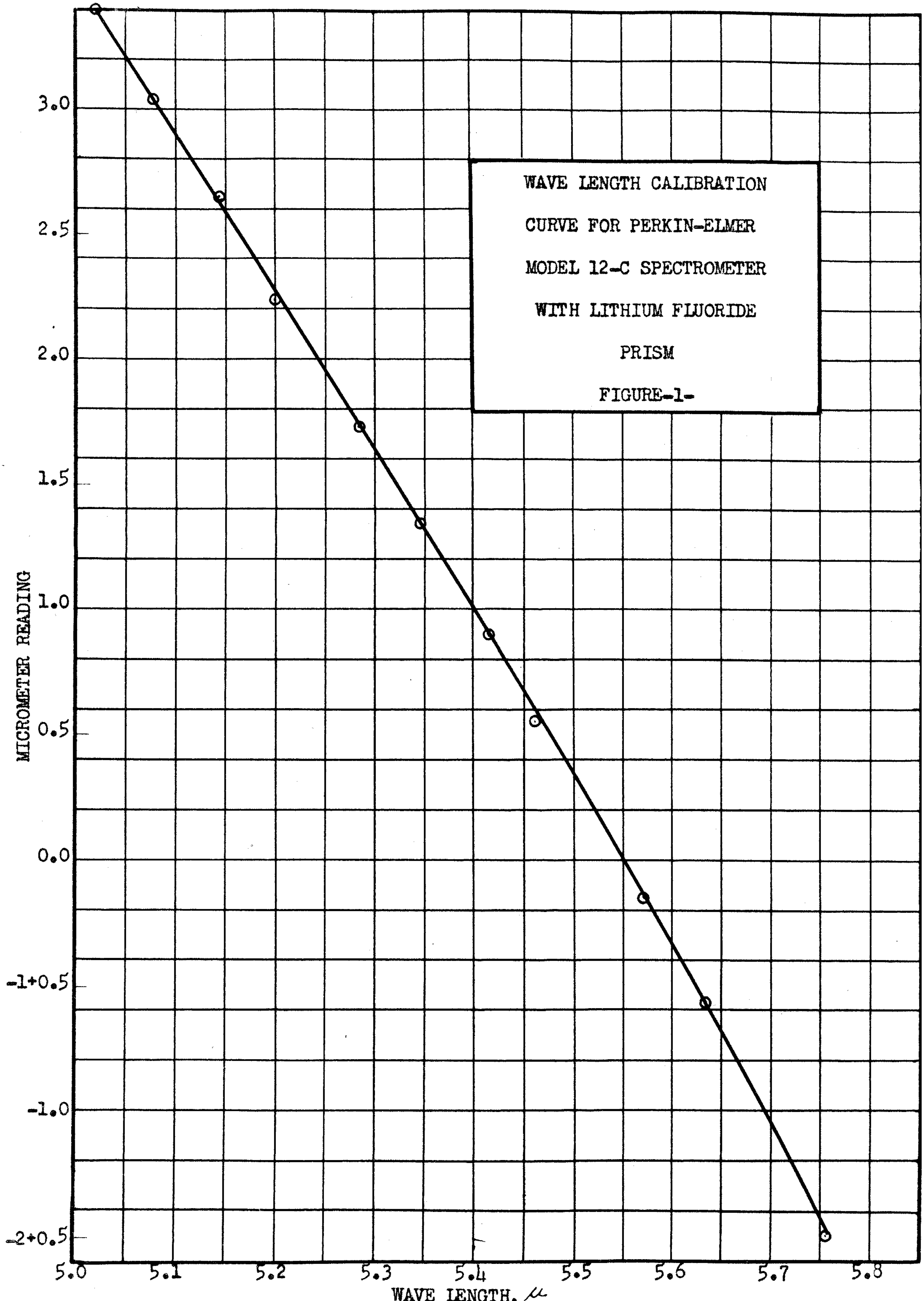
5- Integrated Percentage Absorption as a Function of Pressure for NO.

6-11- The Dependence of j $\exp(-E_{o,j}/kT)$ on j for NO at 300, 1000, 1500, 2000, 2500, 3000°K.

12- Maximum Wave Length Cut-off for the Effective Band Widths of NO as a Function of Temperature.

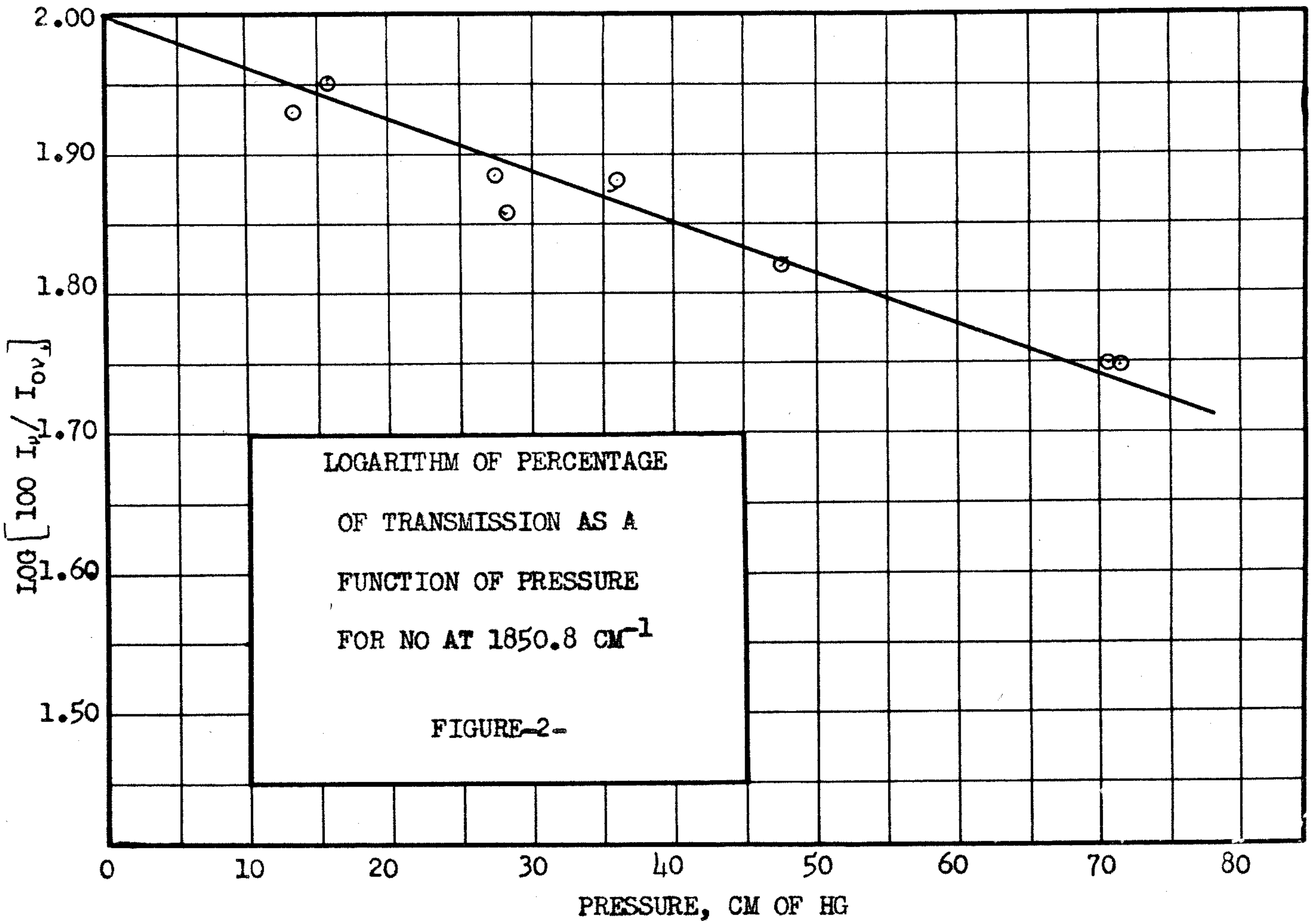
13- Minimum Wave Length Cut-off for the Effective Band Widths of NO as a Function of Temperature.

14- Maximum Contributions to the Total Emissivity from the Fundamental and First Overtone of NO.



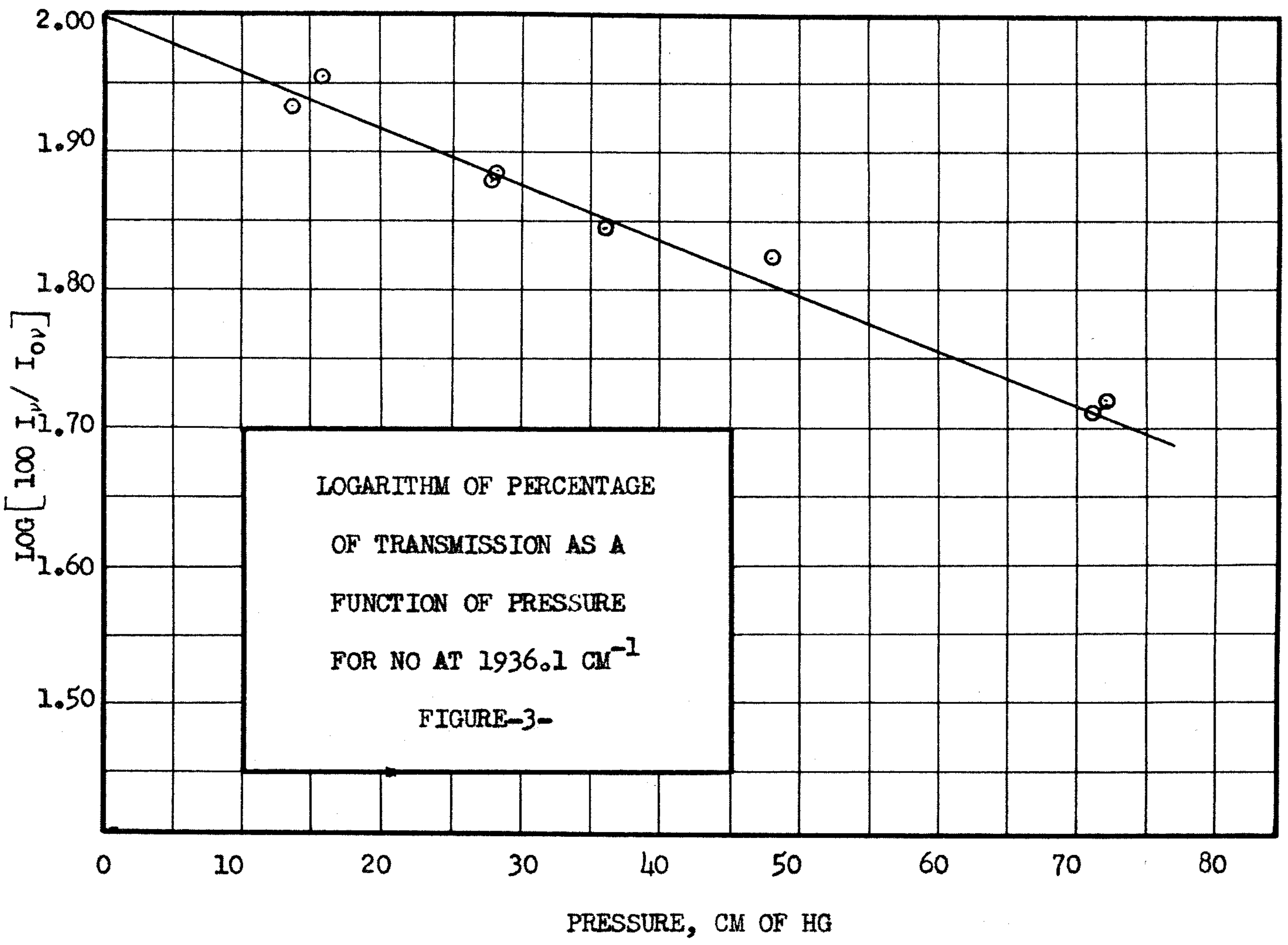
WAVE LENGTH CALIBRATION
CURVE FOR PERKIN-ELMER
MODEL 12-C SPECTROMETER
WITH LITHIUM FLUORIDE
PRISM

FIGURE-1-



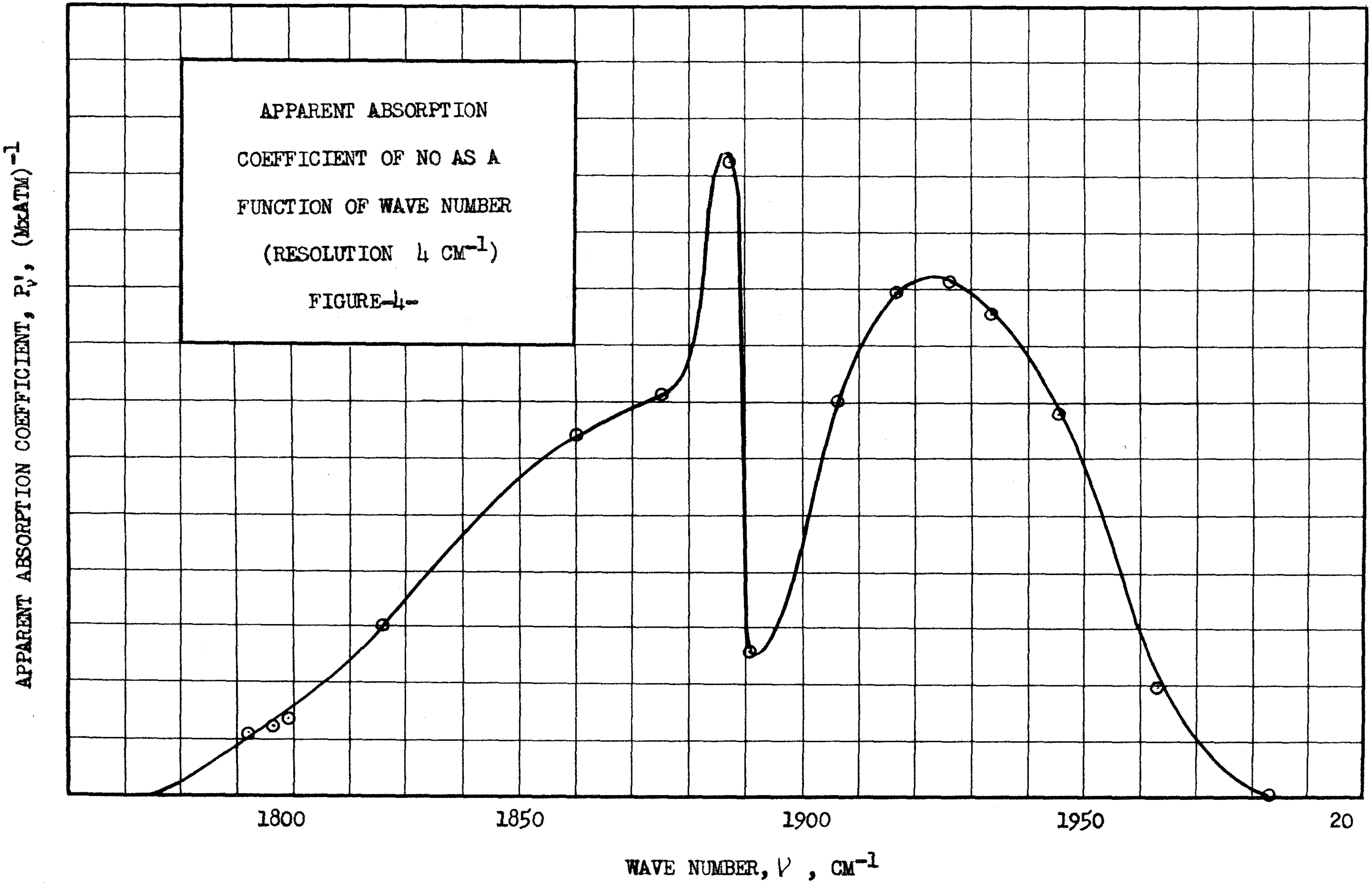
LOGARITHM OF PERCENTAGE OF TRANSMISSION AS A FUNCTION OF PRESSURE FOR NO AT 1850.8 CM^{-1}

FIGURE-2-

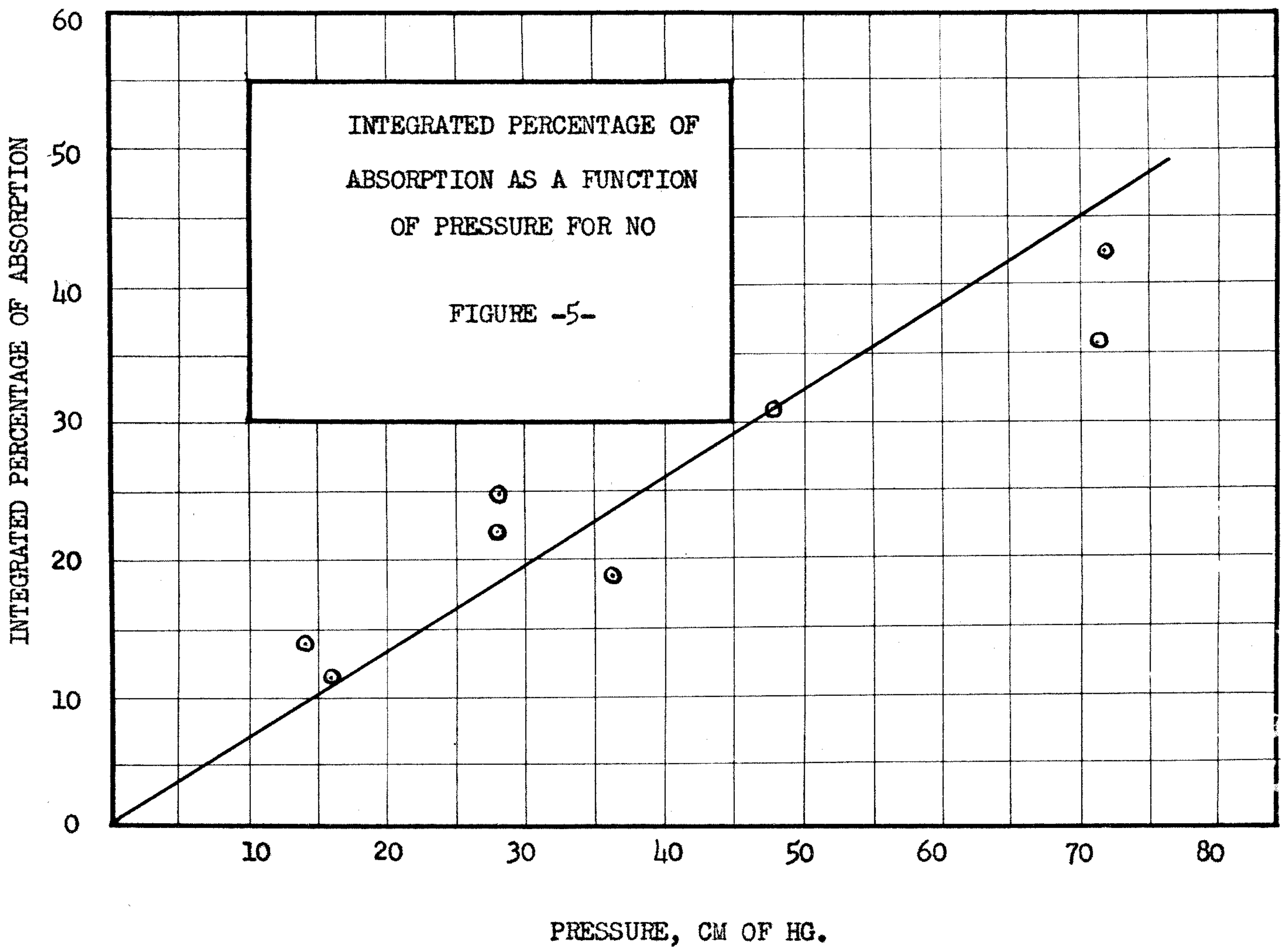


LOGARITHM OF PERCENTAGE OF TRANSMISSION AS A FUNCTION OF PRESSURE FOR NO AT 1936.1 CM^{-1}

FIGURE-3-

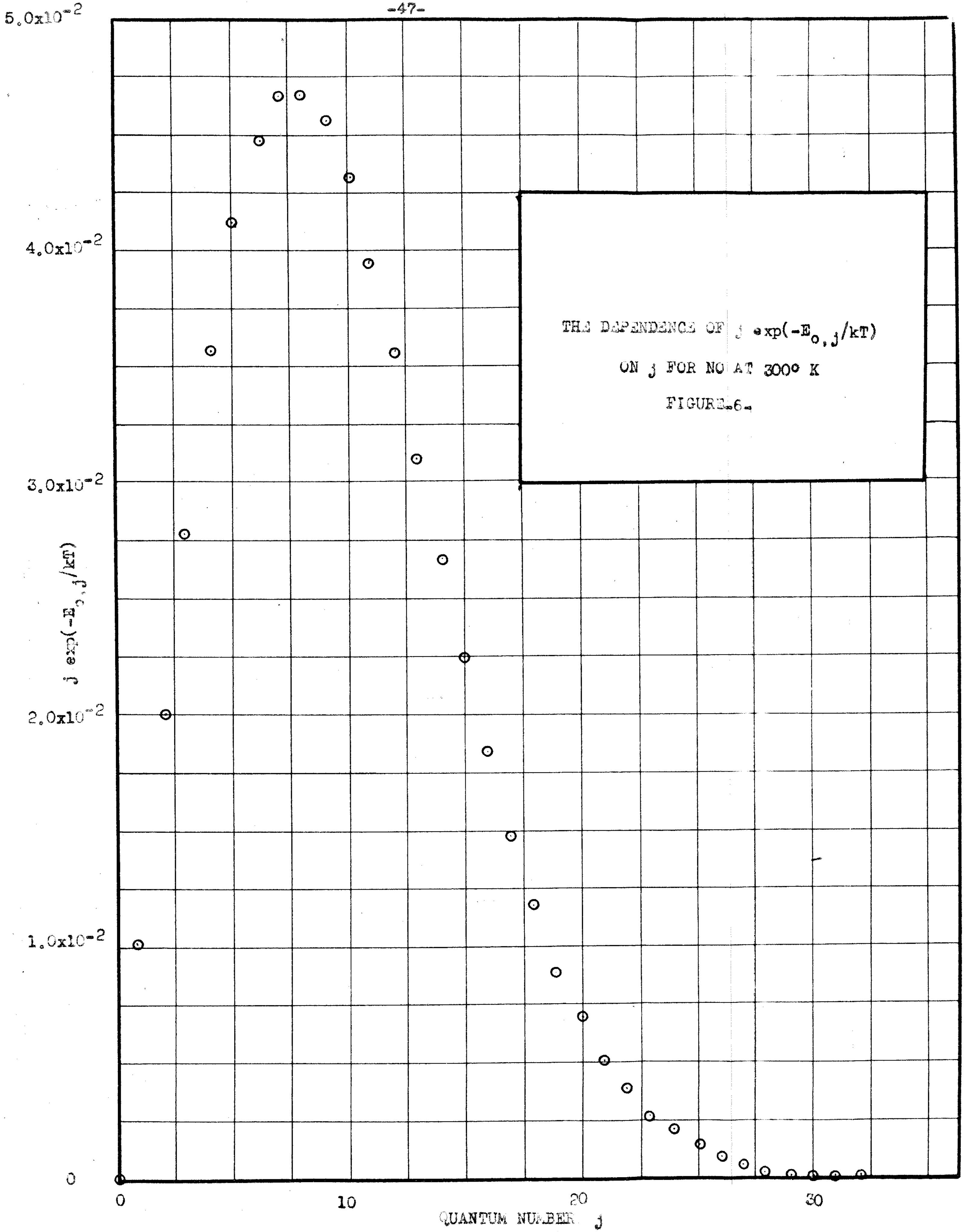


APPARENT ABSORPTION
COEFFICIENT OF NO AS A
FUNCTION OF WAVE NUMBER
(RESOLUTION 4 CM^{-1})
FIGURE-4-



INTEGRATED PERCENTAGE OF ABSORPTION AS A FUNCTION OF PRESSURE FOR NO

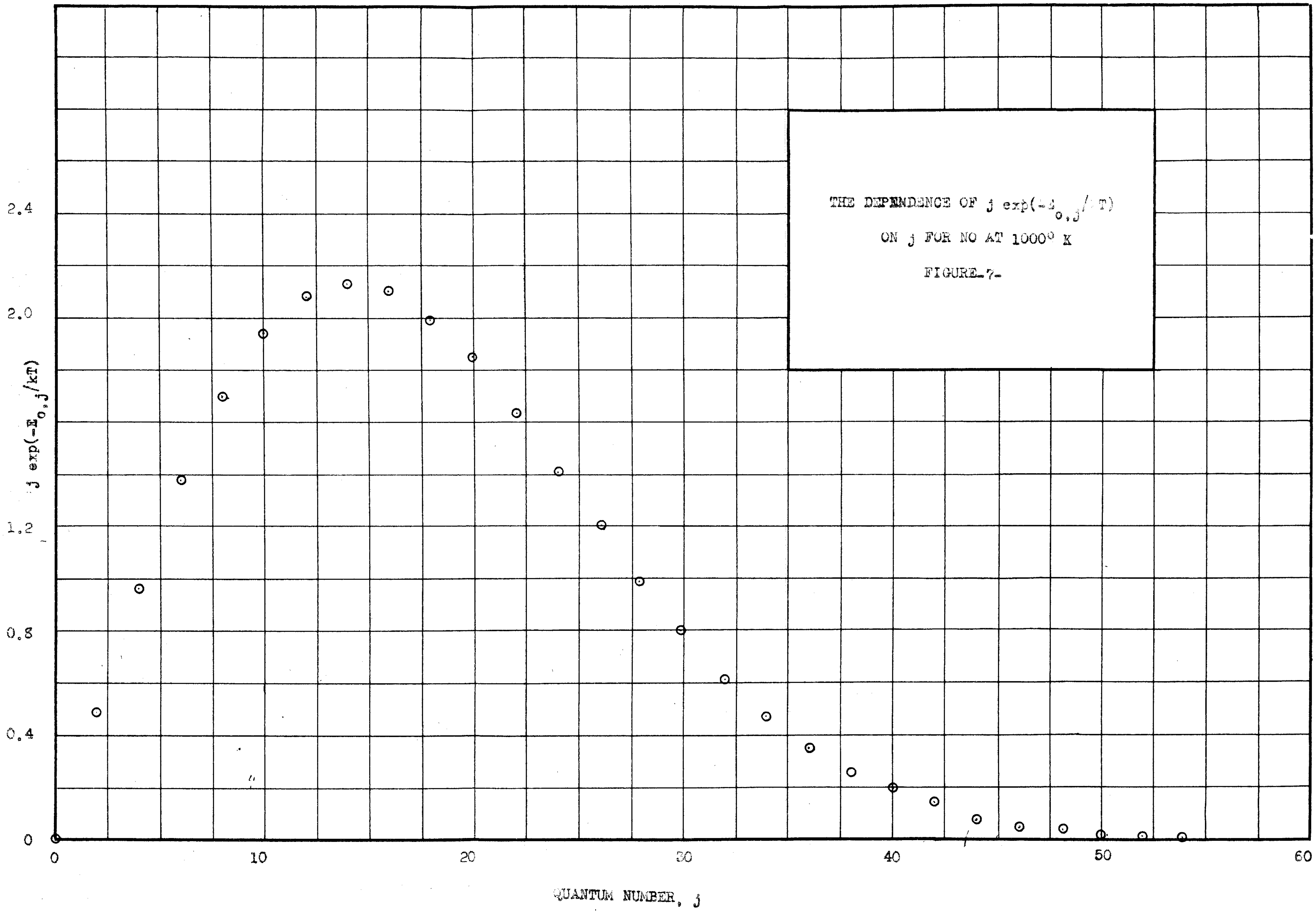
FIGURE -5-



THE DEPENDENCE OF j exp($-E_{o,j}/kT$)

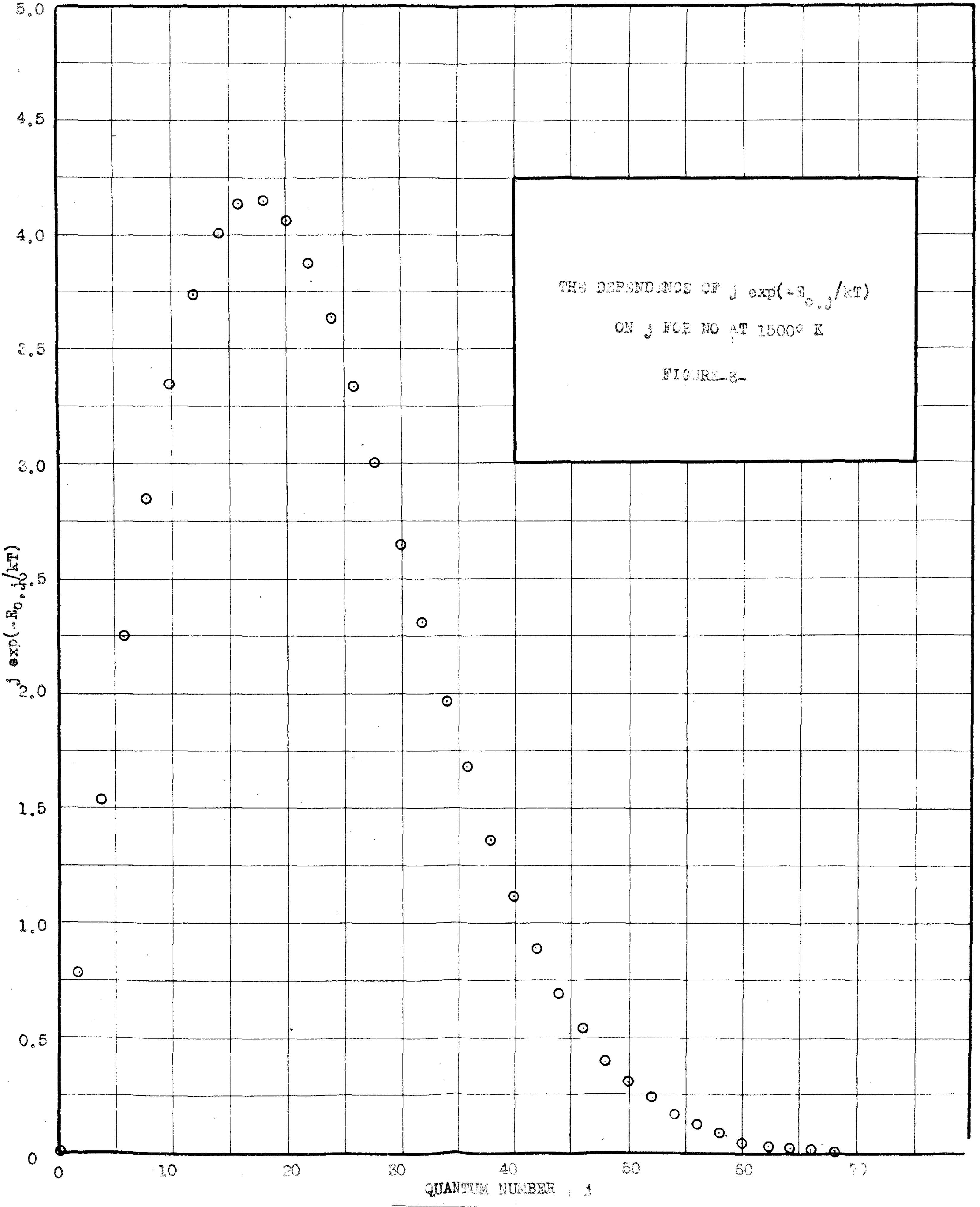
ON j FOR NO AT 300° K

FIGURE 6.



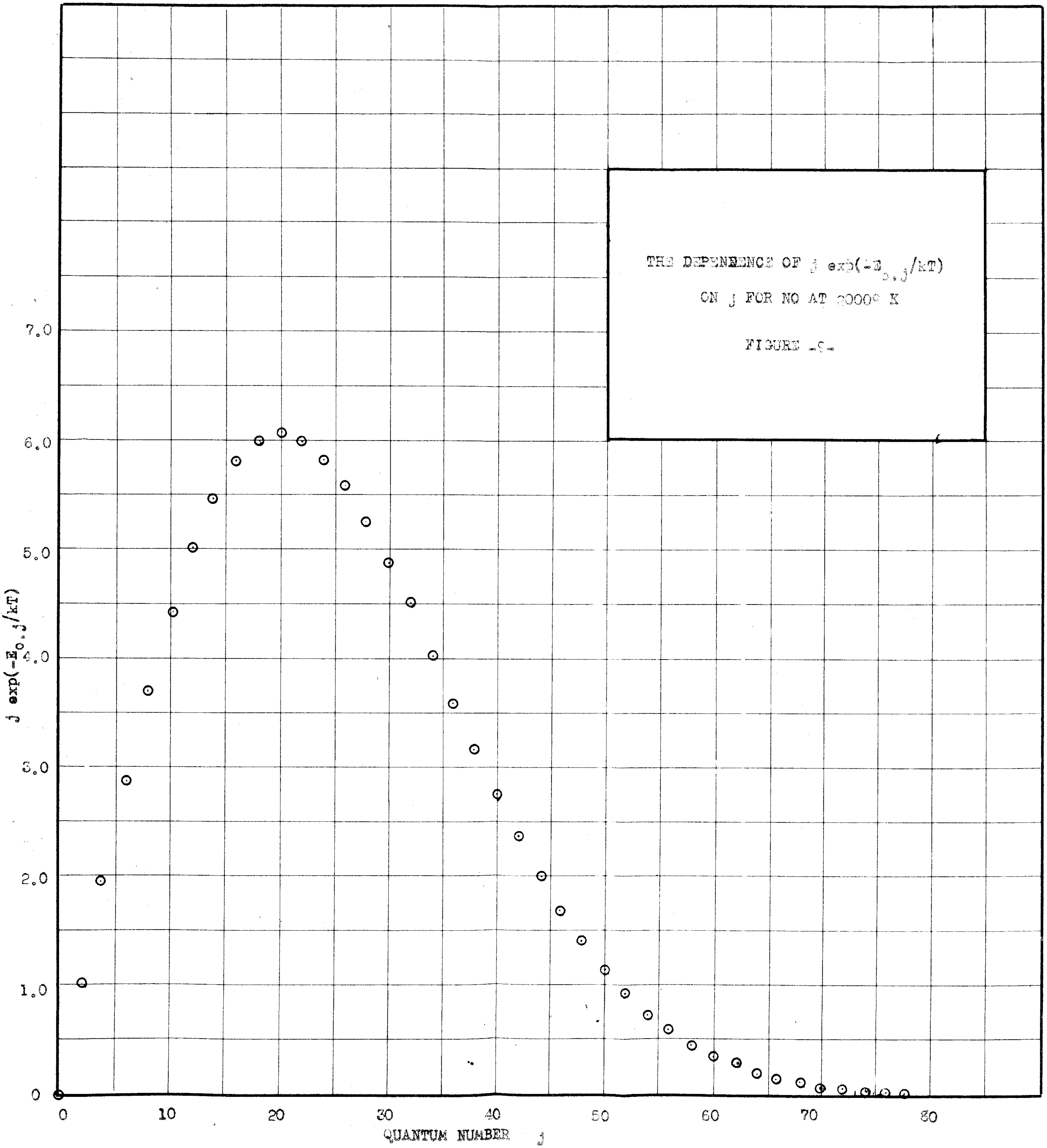
THE DEPENDENCE OF $j \exp(-E_{o,j}/kT)$ ON j FOR NO AT 1000° K

FIGURE-7-



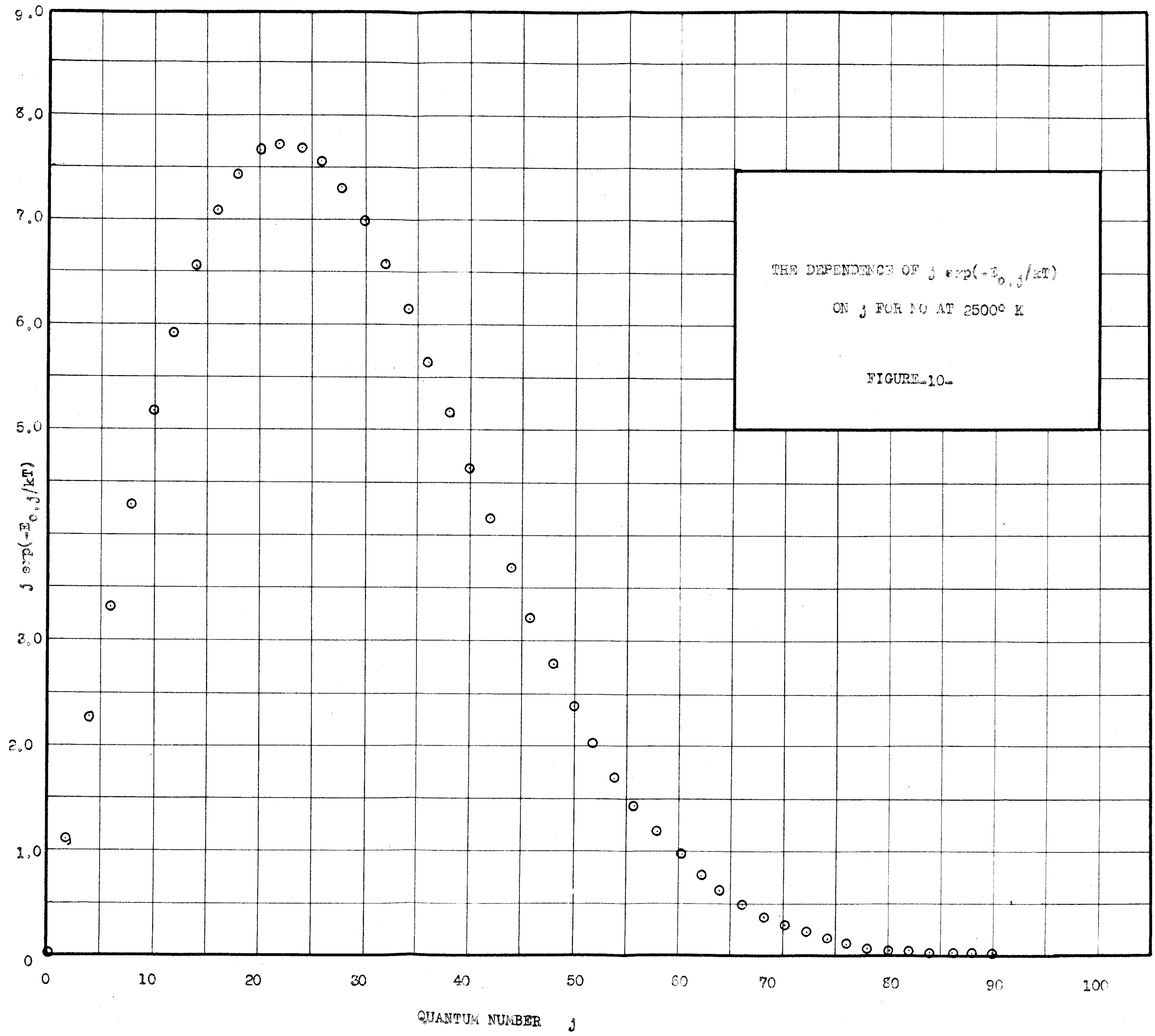
THE DEPENDENCE OF $j \exp(-E_{0,j}/kT)$ ON j FOR NO AT 1500° K

FIGURE-8-



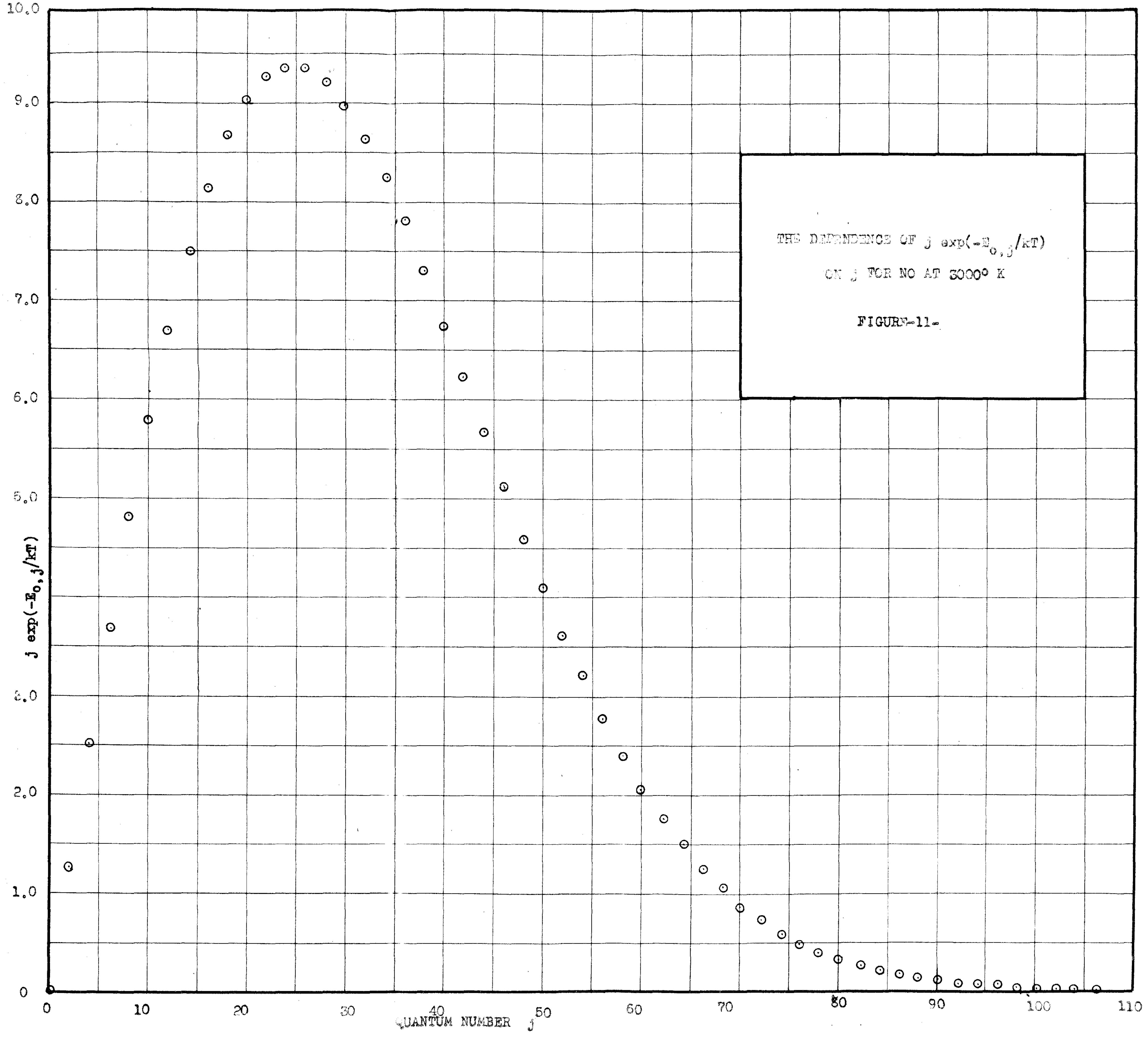
THE DEPENDENCE OF j exp$(-E_{0,j}/kT)$
ON j FOR NO AT 2000° K

FIGURE -9-



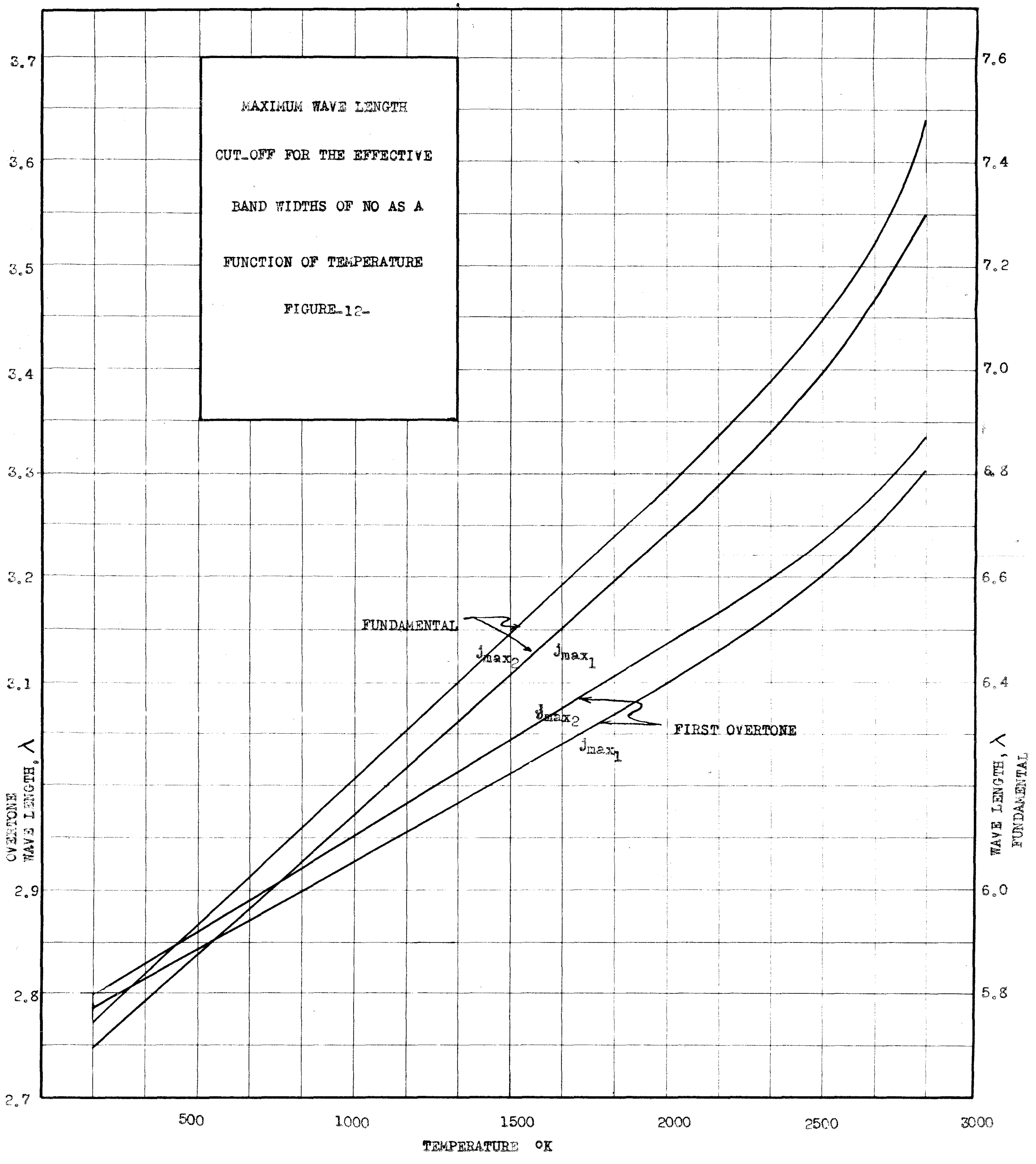
THE DEPENDENCE OF $j \exp(-E_{0,j}/kT)$ ON j FOR NO AT 2500° K

FIGURE 10



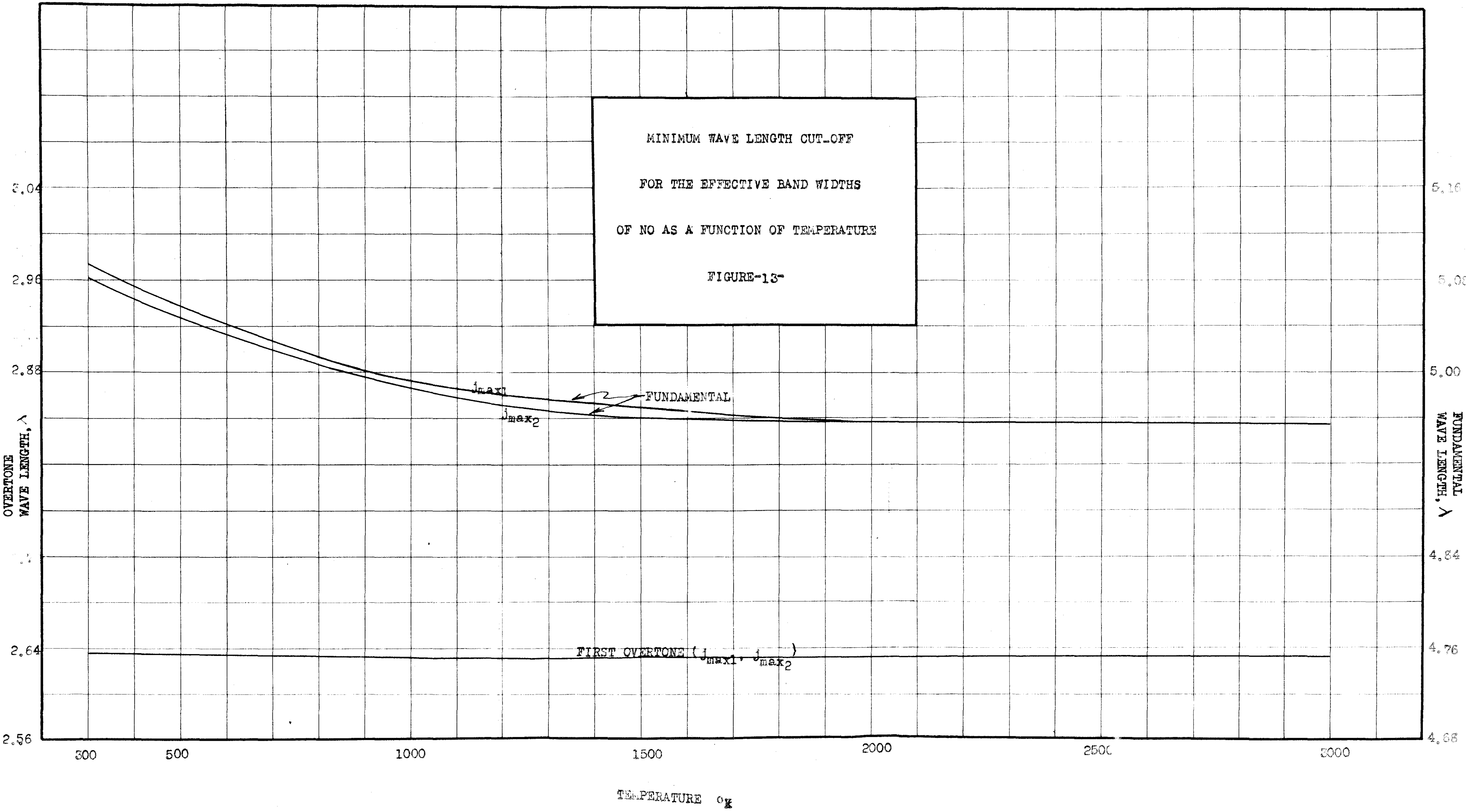
THE DEPENDENCE OF j exp($-E_{0,j}$/kT) ON j FOR NO AT 3000° K

FIGURE-11-



MAXIMUM WAVE LENGTH CUT-OFF FOR THE EFFECTIVE BAND WIDTHS OF NO AS A FUNCTION OF TEMPERATURE

FIGURE-12-

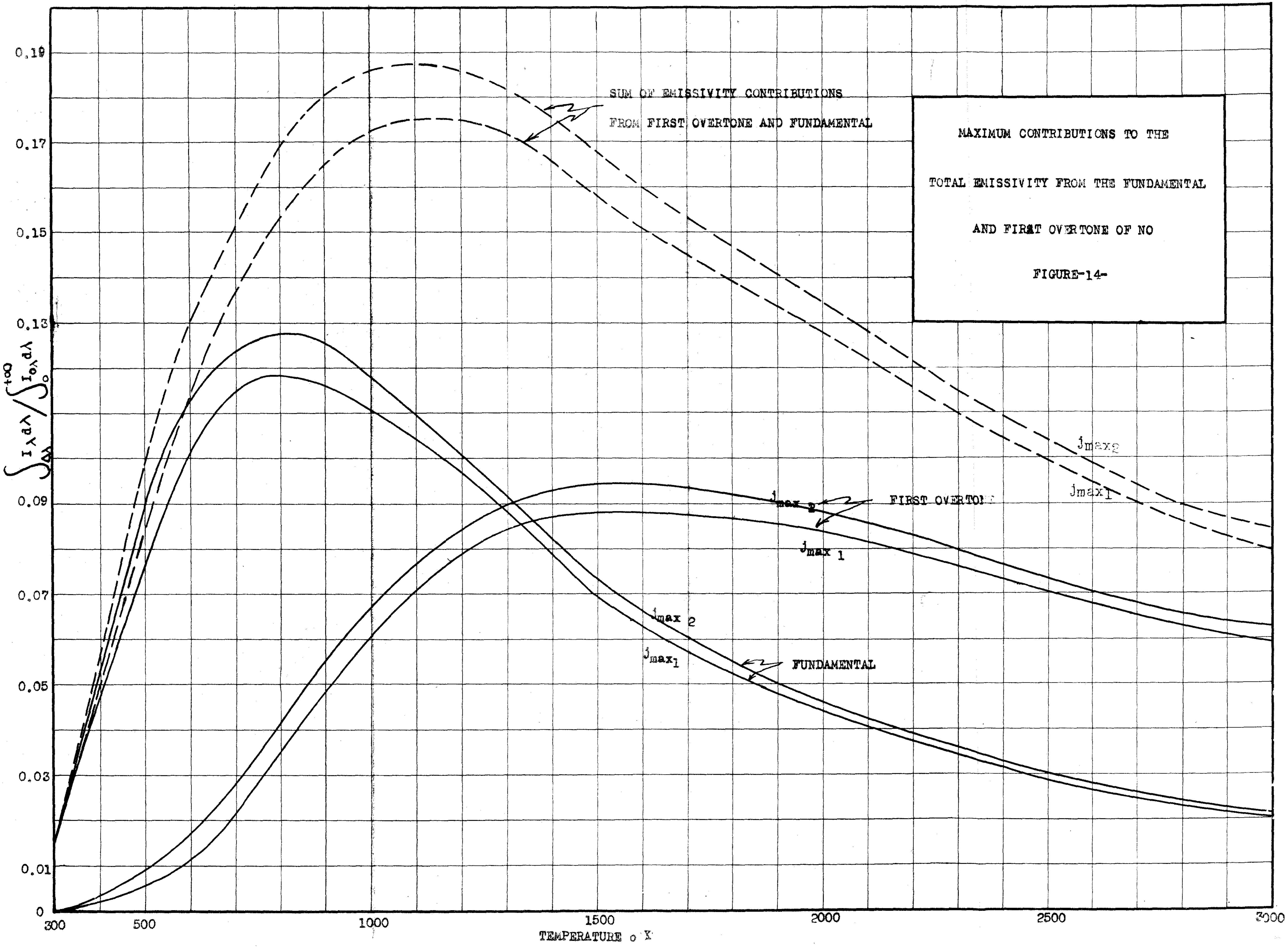


MINIMUM WAVE LENGTH CUT-OFF

FOR THE EFFECTIVE BAND WIDTHS

OF NO AS A FUNCTION OF TEMPERATURE

FIGURE-13-



MAXIMUM CONTRIBUTIONS TO THE TOTAL EMISSIVITY FROM THE FUNDAMENTAL AND FIRST OVERTONE OF NO

FIGURE-14-