

$B \leftarrow N$  system. The latter is well developed at a furnace temperature of 1080°C, while no trace of our present bands is seen below 1150°C. The continuum has stronger absorption, as it begins to appear at the ultraviolet end at temperatures slightly below 1080°C.

Mulliken<sup>1</sup> predicts two transitions for this region,  $V \leftarrow N$  and  $Q_0 \leftarrow N$ , of which the latter should probably give a continuum. The extended system described above is probably to be identified with  $V \leftarrow N$ . The bands are single-headed, as expected, and from the vibrational intensity distribution it can be concluded that  $r_e'$  is considerably greater than  $r_e''$ . This is also attested by some measurements of the rotational structure of the 1,1 band. A distinct series originating at the head could be measured, and followed the equation

$$\nu = 43,451.34 - 0.022M^2.$$

Thirty consecutive lines ( $M=16$  to 46) were measured. The value of  $B' - B''$  is therefore  $-0.022$ , while  $B''$  itself is of the order of  $0.121 \text{ cm}^{-1}$  according to Badger's relation I.<sup>4</sup> The most striking characteristic of our state  $V$ , however, is the fact that although  $r_e$  is much greater than in the normal state,  $\omega_e$  is only very slightly less. Exactly the opposite behavior is observed in state  $B$ , which has nearly the same  $r_e$  as the normal state, but an  $\omega_e$  which is even less than that we find for state  $V$ . These peculiarities of these states agree with the strong interaction between the various curves postulated by Mulliken.

It seems unlikely that our second system is  $Q_0 \leftarrow N$ , because it is so similar to  $V \leftarrow N$ . The strength of the continuum does not seem too great to ascribe it to  $Q_0 \leftarrow N$ .

<sup>4</sup> R. M. Badger, *J. Chem. Phys.* 2, 128 (1930).

## Temperature Determinations from Band Spectral Data

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A method of interpreting intensity distributions of lines in a band for determining the temperature of the emitter has been worked out which is independent of photometer calibration. The criterion used is the place in the band where adjacent lines of overlapping branches are of equal intensity, that is, the intersection of envelopes of the microphotometer records for the respective branches of a given band. The temperature is readily determined from graphs showing the temperature as a function of the  $J$  values at which the simultaneous requirements of equality of intensity and equality of frequency are satisfied in a given

pair of branches. The method has been applied to the (0,1), (0,2), (0,3) and (0,4) bands of the Angstrom system of CO excited in the electrodeless ring discharge, both at room temperature and within a furnace at 365°C. Comparison of thermometer indications with the temperatures obtained by this method indicates (a) that the rotational energy distributions are characteristic of the temperature of the gas in the source, and (b) that the electrodeless ring discharge is a low temperature source of spectra. The error of the new method under favorable conditions may be as small as 5 percent of the absolute temperature.

### INTRODUCTION

THE relative intensities of the lines in a band are determined by the proportionate numbers of molecules in the initial rotational states, and the transition probabilities for the states in question. If thermal equilibrium exists the intensity distribution can be computed from well-known formulas.<sup>1</sup> Even in cases where thermal

equilibrium is obviously not attained, intensities may indicate a distribution of rotational energies corresponding to some effective rotational temperature. In particular, in a glow discharge where electronic bands requiring excitations of several volts are being emitted, the rotational energies may be in equilibrium with the unexcited molecules of the gas at a temperature only slightly above room temperature.

Although band intensity data have been used for estimating temperatures of both celestial and

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<sup>1</sup> W. Jevons, *Report on Band Spectra of Diatomic Molecules* (1932).

terrestrial sources, in only a few instances has the temperature been determined independently by conventional means. The investigation reported here was begun for the purpose of comparing rotational temperatures with thermometer readings in the electrodeless ring discharge maintained at various temperatures. Carbon monoxide gas was chosen for these experiments, because the bands of this molecule are so well known. The results for the Angstrom bands of CO are here presented, and a new method of interpreting the observations which uses the microphotometer essentially as a null instrument is described.

#### EXPERIMENTAL PROCEDURE

A push-pull Hartley oscillator using two RCA 852 tubes operating at a frequency of 20 megacycles was the means of exciting the CO spectra studied. This oscillator was run at a power input of about 450 watts, the plate supply being furnished by a 2000-volt d.c. generator. The entire oscillator, including the tank coil within which the discharge tube was placed, was enclosed in a metal shield which limited radio-frequency radiation from the oscillator, thereby protecting sensitive devices elsewhere in the building.

The discharge tube had a plane quartz window and a quartz-to-Pyrex graded seal on one end, and a connection to the gas generator and vacuum system at the other end. The furnace around the discharge tube and tank coil was made up of double walls of asbestos board, with two 30 ohm, Nichrome heating units connected in parallel to the 110 volt a.c. line. Openings were provided for the light from the window and for the connection to the vacuum system. Temperatures were observed by simply placing a mercury thermometer within the tank coil near the discharge tube. With the heating current turned off, the enclosure nevertheless was hotter than room temperature because of heating by the discharge.

Carbon monoxide was produced by passing the vapor from concentrated formic acid (HCOOH) at reduced pressure over  $P_2O_5$ , which dehydrated the formic acid with the evolution of CO, and also eliminated most of the water vapor. A trap cooled by liquid air or dry ice removed all traces

of vapor contaminations and no foreign spectra appeared in the CO discharge after baking the discharge tube and flushing it out several times with gas from the generator.

The gas generator and discharge tube were exhausted by means of a mercury diffusion pump backed by a Hyvac pump. A McLeod gauge was used to measure pressures. During a run the pumps were operated against a slow leak through a stopcock adjusted to maintain the desired pressure. This was held at an average value of 0.091 mm of Hg, with mean fluctuation of 0.003 mm, for an exposure of five hours.

Spectrograms were obtained by means of a 21-foot, 30,000 lines per inch grating in a Paschen-Runge mounting. This instrument has a mean dispersion in the visible wave-length range of 1.3 Å/mm in the first order. For the region 2500–7000 Å in the first order Eastman 40 and hypersensitive panchromatic plates were used. The particular bands studied lie at the wave-lengths 4835, 5198, 5610, and 6080 Å. The slit was mounted at 13° from the normal to the grating, for minimum astigmatism.<sup>2</sup>

Microphotometer traces for the bands investigated were made with a Moll, thermoelement instrument. The region covered by a single record was sufficient to include all the significant lines of a single band. For the purposes of this study, explicit intensity data were not required, and the indications of the microphotometer could be used without reducing them to true intensities, hence calibrations of the plates and of the photometer were dispensed with. In the following discussion, microphotometer deflections will occasionally be referred to as intensities for the sake of concise expression.

#### TEMPERATURE DETERMINATIONS

##### Theory of band-line intensities

The intensity of a line in a band may be represented<sup>1</sup> by

$$I = \text{const. } \nu^4 i e^{-E_r/kT} \quad (1)$$

if temperature equilibrium exists among the excited molecules at an absolute temperature,  $T$ . In this expression  $i$  is the intensity factor which

<sup>2</sup> H. Newhouse, Master's Thesis, Ohio State University (1935).

depends on the quantum-mechanical transition probability for the given line,  $E_r$  is the rotational energy of the initial state, and  $k$  is the Boltzmann constant. The constant of Eq. (1) holds for all branches of a particular band.

The Angstrom band system arises from transitions between the  $B^1\Sigma$  and  $A^1\Pi$  levels of CO. In each of these bands, extending for only a small wave-length range, the frequency factor,  $\nu^4$ , may be considered constant. From wave mechanics the value of  $E_r$  is found to be  $B_v hcJ(J+1)$  where  $B_v$  is the well-known molecular constant for the vibrational level in question,  $h$  is Planck's constant,  $c$  is the velocity of light in vacuum, and  $J$  is the rotational quantum number. By means of the intensity factors derived by Hönl and London<sup>3</sup> the following expressions are obtained for the intensities of the three branches of any one of these bands expressed in terms of the rotational quantum numbers of the final level:

$$I_P(J'') = \text{const.} (J''+1) \cdot \exp - (B_v' hc J''(J''-1)/kT), \quad (2)$$

$$I_Q(J'') = \text{const.} (2J''+1) \cdot \exp - (B_v' hc J''(J''+1)/kT), \quad (3)$$

$$I_R(J'') = \text{const.} (J'') \cdot \exp - (B_v' hc (J''+1)(J''+2)/kT), \quad (4)$$

$$J'' = 1, 2, 3, 4, \dots$$

The value of  $B_v'$  for the Angstrom bands studied here, which arise from the lowest vibrational state of the initial level,  $B^1\Sigma$ , is given by Hulthén<sup>4</sup> as  $1.942 \text{ cm}^{-1}$ .

#### Temperature from intensity maxima

The earliest use of the intensities of band lines for temperature estimates preceded the derivation of intensity expressions according to the new quantum theory, hence some of the analytical expressions used differ slightly from the relations accepted at present. However, the results are essentially the same.

By picking out the line of maximum intensity in a particular branch of a CN band, Birge<sup>5</sup> obtained temperatures of  $70^\circ\text{C}$  for active nitro-

gen,  $4000^\circ\text{C}$  for the solar reversal layer, and  $3900^\circ\text{C}$  to  $4500^\circ\text{C}$  for an arc with various currents and voltages. For the temperature of the underwater spark Wilson<sup>6</sup> found a value of  $5000^\circ\text{C}$  from the OH bands in absorption. In the case of the SiN bands excited by an active nitrogen source Mulliken<sup>7</sup> deduced a temperature of  $80^\circ\text{C}$  from the intensity maxima, which compares well with the value found by Birge for an active nitrogen source. Subsequently, Barton, Jenkins, and Mulliken<sup>8</sup> determined temperatures ranging from  $290^\circ\text{K}$  to  $330^\circ\text{K}$  from the beta-bands of NO as excited by active nitrogen.

More recently, by the use of the corrected formulas and quantum numbers, Johnson and Turner<sup>9</sup> found a rotational temperature of  $750^\circ\text{K}$  for the bands of  $\text{He}_2$  excited by a condensed discharge. Richardson<sup>10</sup> studied temperatures in sunspots and in the reversing layer of the sun by applying this method to the Swan band of  $\text{C}_2$  at  $5165\text{Å}$ .

It is obvious that the selection of the line of maximum intensity is independent of microphotometer calibration, and is thus convenient for such temperature measurements. However, the envelope at the maximum intensity is comparatively flat, and the maximum shifts only slightly with large changes in temperature. Hence, misinterpretations may arise because of these conditions and because of the blending of lines.

Expressions for the temperature in terms of the  $J$  values of the lines having greatest intensities in the different branches may be found by setting the first derivatives of the relations (2)–(4) equal to zero and simplifying. In Fig. 1 the graphs of these relations for the Angstrom bands which have the common initial vibrational state,  $v'=0$ , have been arranged. From the curves drawn there one may see that a change in temperature of  $100^\circ$  should change the point of maximum intensity by approximately one unit on the  $J''$  scale for values in the neighborhood of  $500^\circ\text{K}$ .

<sup>6</sup> E. D. Wilson, J. O. S. A. and Rev. Sci. Inst. **17**, 37 (1928).

<sup>7</sup> R. S. Mulliken, Phys. Rev. **26**, 319 (1925).

<sup>8</sup> H. A. Barton, F. A. Jenkins and R. S. Mulliken, Phys. Rev. **30**, 175 (1927).

<sup>9</sup> R. C. Johnson and R. C. Turner, Proc. Roy. Soc. **A142**, 574 (1933).

<sup>10</sup> R. S. Richardson, Astrophys. J. **73**, 216 (1931).

<sup>3</sup> H. Hönl and F. London, Zeits. f. Physik **33**, 803 (1925).

<sup>4</sup> E. Hulthén, Ann. d. Physik **71**, 41 (1923).

<sup>5</sup> R. T. Birge, Astrophys. J. **55**, 273 (1922).

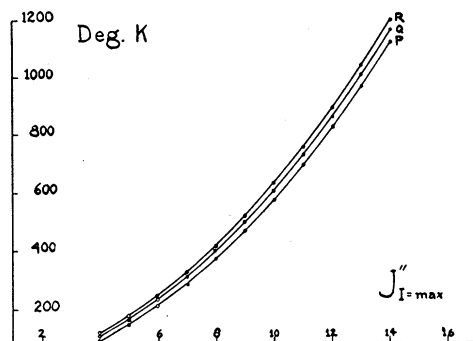


FIG. 1. Temperatures at which various  $J''$  values designate lines of maximum intensity, computed for the  $P$ ,  $Q$ , and  $R$  branches of Angstrom bands arising from the  $v'=0$  level of the initial electronic state.

### Temperature from intensity factor graphs

From the Eq. (3) it may be seen that a graph of  $\ln [I_Q(J'')/(2J''+1)]$  against  $J''(J''+1)$  should be a straight line of slope  $(-B_v/hc/kT)$ . This was introduced by Ornstein and van Wijk<sup>11</sup> as a method for measuring temperatures. In applying it to the light from an electric arc these investigators obtained a temperature of 5000°K from the CN bands and 2800°K from the bands of aluminum oxide. A comparison of the values found from the CN and  $C_2$  bands simultaneously emitted by discharges through  $CH_4$  and  $C_2H_2$  was made by Lochte-Holtgreven.<sup>12</sup> Horst and Krygsman<sup>13</sup> made similar observations on the bands of these molecules as obtained by discharges in air. The same type of analysis has been applied in measuring effective discharge temperatures from bands of mercury hydride<sup>14</sup> and nitrogen,<sup>15</sup> and arc temperatures from the violet cyanogen and aluminum oxide bands<sup>16, 17</sup> The nitrogen band at 3914Å was the subject of the studies made by Lindh<sup>18</sup> and by Thompson<sup>19</sup> for

<sup>11</sup> L. S. Ornstein and W. R. van Wijk, *Zeits. f. Physik* **49**, 315 (1928).

<sup>12</sup> W. Lochte-Holtgreven, *Zeits. f. Physik* **64**, 443 (1930); **67**, 590 (1931).

<sup>13</sup> D. Th. J. ter Horst and C. Krygsman, *Physica* **1**, 114 (1933).

<sup>14</sup> W. Kapuściński and J. G. Eymers, *Zeits. f. Physik* **54**, 246 (1929).

<sup>15</sup> L. S. Ornstein and P. J. Haringhuizen, *Zeits. f. Physik* **77**, 788 (1932).

<sup>16</sup> L. S. Ornstein and H. Brinkman, *Proc. K. Akad. Amst.* **34**, 33 (1931).

<sup>17</sup> L. S. Ornstein and W. R. van Wijk, *Proc. K. Akad. Amst.* **33**, 44 (1930).

<sup>18</sup> A. E. Lindh, *Zeits. f. Physik* **67**, 67 (1931).

<sup>19</sup> N. Thompson, *Proc. Phys. Soc.* **46**, 436 (1934); **47**, 413 (1935).

various excitation conditions in the low voltage arc, and the temperature of exploding aluminum wires was determined by Nagashima<sup>20</sup> from the AlH band at 4241Å by means of this method.

Lochte-Holtgreven and Maecker<sup>21</sup> have pointed out certain influences which will distort such graphs. Surprisingly high temperatures have been derived in this manner by several investigators, and disagreement as to the interpretation of the true slope is found in some of the cited papers.

An application of this analysis for determining rotation temperatures requires accurate measurement of the individual line intensities using all the precautions essential to photometry of spectral lines. At best the method is very tedious to apply since so many quantities must be measured.

### Temperature from frequency intensity equalities

In examining microphotometer records of an Angstrom band produced at two different temperatures, it was noticed that adjacent lines of the  $Q$  and  $R$  branches reached equal intensity in the tail of the band at room temperature, but at a higher temperature the place at which the two branches became equal in intensity occurred still farther away from the band origin. This observation suggested the possibility of using such points as a criterion for evaluating the rotational temperature. It has been found that the  $P$  and  $R$  branches also yield such a criterion.

If the envelopes for the microphotometer deflections are drawn for the respective branches, the points of intersection of the envelopes for the  $P$  and  $R$  branches will be points at which the conditions are simultaneously satisfied:

$$\nu_P = \nu_R, \quad (5)$$

$$I_P = I_R. \quad (6)$$

The frequencies and intensities may both be considered as continuous functions of  $J$ , the rotational quantum number for the lower level, since the observed  $J$  values,  $J_R$  and  $J_P$ , which satisfy these equations will not in general be integral numbers.

To find the temperature corresponding to an observed intersection the frequency equation

<sup>20</sup> H. Nagashima, *Tokyo B. D. Sci. Reports, Sec. A1*, 219 (1932).

<sup>21</sup> W. Lochte-Holtgreven and H. Maecker, *Zeits. f. Physik* **105**, 1 (1937).

symbolized by (5) may be solved for one of the  $J$  values in terms of the other one alone. Substitution in the equation symbolized by (6) would then give an expression involving only the temperature and one  $J$  value of the intersection. Hence, the temperature is the only unknown if the value of either  $J$  at the intersection is determined from the observed band.

In practice, it is more convenient to proceed graphically. First, from a conventional Fortrat diagram, or from a plot of  $J$  numbers against wave-length, the value of  $J_P$  satisfying (5) can be found for any  $J_R$ . Next, a graph of temperatures against  $J_R$  may be prepared by substituting in Eq. (6) the various pairs of  $J$  values found in this manner. From this graph the temperature may be read directly, as soon as the  $J$  value of the intersection is found on the microphotometer record.

In order to test the accuracy of this procedure, temperatures were obtained from the intersections found on graphs of computed intensities plotted against wave-length, as in Fig. 2. These temperatures were compared with the values used in computing the plotted intensities, for the Angstrom (0,3) band at 5610A. The temperatures obtained by the method outlined came within one percent of the assumed values. This error is negligible in comparison with the error produced by the uncertainty in drawing the intensity envelopes.

In general, in a band with three branches there will be three intersections of intensity envelopes. For bands of the type considered here, the rotational temperature,  $T^\circ\text{K}$ ., corresponding to each

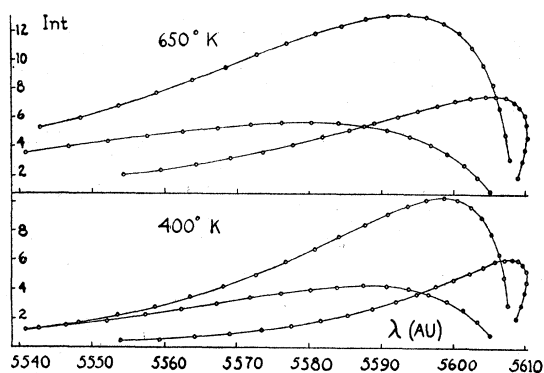


FIG. 2. Calculated intensities at temperatures of 650°K (above) and 400°K (below) for the lines of the Angstrom (0,3) band at  $\lambda 5610$ , plotted against wave-length. Compare with microphotometer records, Fig. 4. An arbitrary scale of intensities is used.

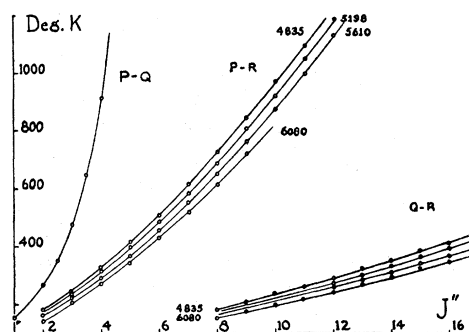


FIG. 3. Relationship between temperature and the  $J$  values of the intersections. For the  $P-R$  and  $Q-R$  curves, the abscissae are values of  $J''(R)$ ; for the  $P-Q$  curve,  $J''(Q)$ . Computed for the Angstrom bands (0,1)  $\lambda 4835$ , (0,2)  $\lambda 5198$ , (0,3)  $\lambda 5610$ , and (0,4)  $\lambda 6080$ .

of these intersections is found by inserting in Eq. (6), and similar ones for the other intersections, the explicit formulas for intensities, and solving to obtain:

$$T = (B_v'hc/k) \cdot [J_P(J_P-1) - J_Q(J_Q+1)] / \ln [(J_P+1)/(2J_Q+1)], \quad (7)$$

$$T = (B_v'hc/k) \cdot [J_P(J_P-1) - (J_R+1)(J_R+2)] / \ln [(J_P+1)/J_R], \quad (8)$$

$$T = (B_v'hc/k) \cdot [J_Q(J_Q+1) - (J_R+1)(J_R+2)] / \ln [(2J_Q+1)/J_R], \quad (9)$$

where  $J_P$ ,  $J_Q$ , and  $J_R$  refer to the  $J''$  values at the intersections, which will not generally be integers but interpolations between the values belonging to the lines on either side of the intersection.

Graphs of Eqs. (7)–(9) are shown in Fig. 3 for four bands of the Angstrom system, except that for the  $P-Q$  intersection the curve is drawn for the 5610A, (0,3) band only, since the curves for the other three bands are very nearly coincident with this curve. From these graphs an impression may be gained of the sensitivity of this criterion to temperature changes.

## RESULTS AND DISCUSSION

In Fig. 4 are shown two microphotometer traces of the 4835 (0,1) Angstrom band at ambient temperatures of 383° and 633°K respectively, illustrating the envelopes drawn, and showing intersections at  $A$ ,  $B$  and  $C$  for the lower temperature, and  $A'$  and  $B'$  for the higher temperature, the  $Q-R$  intersection being hidden in the

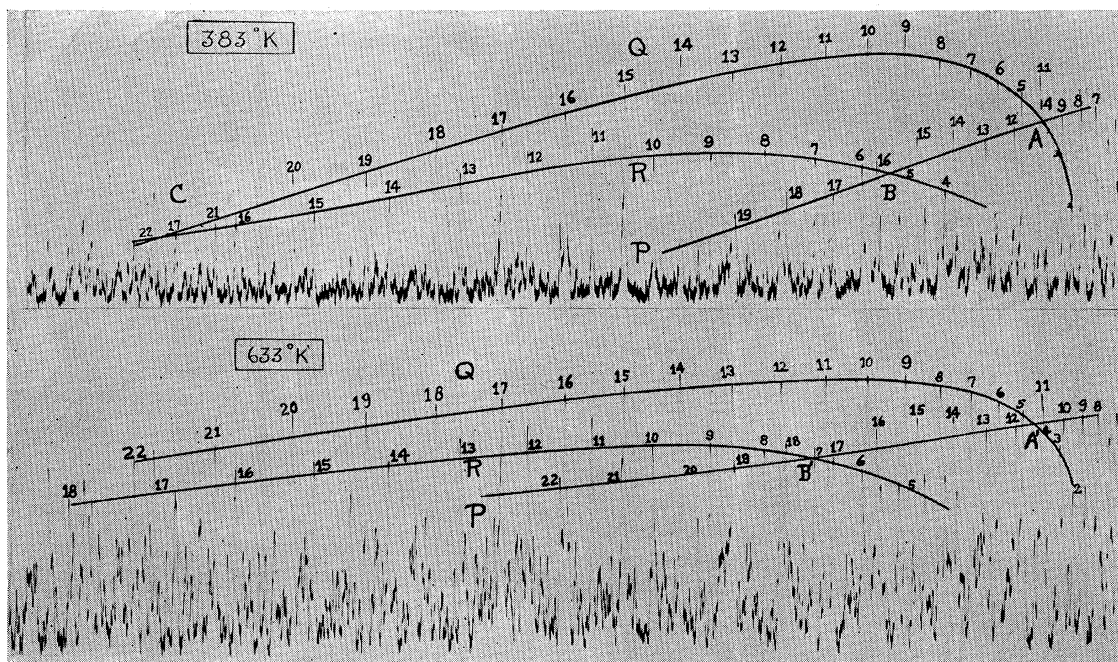


FIG. 4. Microphotometer records of the Angstrom band (0,1)  $\lambda 4835$ , showing  $P$ - $Q$  intersections at  $A, A'$ ;  $P$ - $R$  intersections at  $B, B'$ , and  $Q$ - $R$  intersection at  $C$ . Above, furnace cold; below, furnace hot.  $J$  values are given for the band lines.

background under the latter conditions. The band degrades toward the violet; that is, the wave-length increases toward the right. Attention is called to the way in which the envelopes are drawn, so as to touch the tops of the *less intense* lines. This procedure is based on the assumption that, in the absence of marked perturbations, no reason is known for finding a line less intense than called for by the formulas, but an excess intensity is quite probable, because of overlapping or "background." It will be noted that the  $P$ - $Q$  intersection, at  $A$  and  $A'$ , is near the head of the band where overlapping of the lines is prevalent; hence this intersection is not well adapted for temperature determinations. The  $Q$ - $R$  intersection is unsuitable at the higher temperature. The  $P$ - $R$  intersection is quite definite, and independent evaluations on duplicate microphotometer traces led to values of  $J$  differing by no more than 0.5, corresponding to temperature differences of  $45^\circ$ . If repeated trials are made, the average deviations indicate that the probable error is considerably less.

In Table I data are presented for four bands on each of four sets of plates, each plate consisting

of a long and a short exposure, the latter being secured by covering up half of the plate during about four-fifths of the duration of the entire exposure. Rotational temperatures are entered for all the observed  $P$ - $R$  intersections, and also for the  $J$  values of the maximum intensities of the  $Q$  branches. The mean values of the temperatures for a given set of conditions are shown, and also the average deviations both for the respective methods and for the respective bands. The temperatures indicated in the first column are readings of a thermometer placed within the furnace and helix against the outside of the discharge tube.

For comparison with furnace temperature, the rotational values under given conditions when averaged are found to be  $88^\circ$  higher with the furnace cold, and  $8^\circ$  lower with the furnace hot. The latter difference is less than the error in the rotational temperature, hence the conclusion is that the rotational temperature is characteristic of the furnace temperature when the latter is  $638^\circ\text{K}$ . For the "cold" furnace,  $353^\circ$  or  $383^\circ\text{K}$ , the temperature within the discharge tube may actually be that indicated by the rotational dis-

tribution, because of heating within the tube by the discharge itself, which absorbed about 300 watts from the oscillator.

The plates listed last in Table I were made with a considerable proportion of CO<sub>2</sub> in the discharge, to see if an anomalous distribution of rotational energies might be observed, produced by a process of simultaneous dissociation of the CO<sub>2</sub> molecule and excitation of the CO fragment. No such anomalies were observed, but the proportion of CO<sub>2</sub> was not controlled well enough to justify a conclusion that such an effect does not exist. Oldenberg<sup>22</sup> has studied this phenomenon in OH excited simultaneously with its dissociation from H<sub>2</sub>O.

The experiments suggest that the intersections of microphotometer envelopes indicate rotational temperatures with an accuracy comparable with those found from locating maxima. However, the intersections can be located more conveniently,

<sup>22</sup> O. Oldenberg, Phys. Rev. **46**, 210 (1934).

and they remain evident on plates which have been overexposed to the point where many lines in the region of the maximum are intense enough to reduce the galvanometer deflection uniformly to zero. Under suitable conditions, both criteria can be applied as they have been here, and the average values thereby have a probable error reduced by 2<sup>-1/2</sup> in comparison with those from either criterion alone.

Reasons for abnormal distributions of intensities in bands have been considered by Lochte-Holtgreven and Maecker<sup>21</sup> with reference to bands from an arc in air at atmospheric pressure. The reasons are: (1) overlapping of lines; (2) inhomogeneity of temperature; (3) self-absorption by gas surrounding the discharge; and (4) self-reversal by cooler layers of gas, resulting in a change in the line contour because of the smaller Doppler widths of the lines absorbed by the cooler molecules. The first of these is clearly unavoidable unless bands with very open structure can

TABLE I. Data on temperature measurements.

TYPE OF DISCHARGE	METHOD OF MEASUREMENT	PORTION OF SPECTROGRAM	TEMPERATURE (DEG. K)					MEAN DEV. FROM MEAN
			4835 BAND	5198 BAND	5610 BAND	6080 BAND	AVERAGE	
CO at 638°K	From Q Branch Maxima	Strong	635	670	635	610	631	16
		Weak	619	615	—	—		
	P-R Intersections	Strong	616	660	585	—	629	32
		Weak	606	680	—	—		
CO at 383°K	Q Branch Maxima	Strong	500	450	400	500	477	32
		Weak	520	477	495	—		
	P-R Intersections	Strong	435	470	420	500	457	27
		Weak	470	480	420	—		
CO at 353°K	Q Branch Maxima	Strong	—	480	400	400	453	45
		Weak	500	500	490	400		
	P-R Intersections	Strong	440	455	385	435	423	39
		Weak	455	455	395	365		
CO <sub>2</sub> at 383°K	Q Branch Maxima	Strong	500	500	500	425	484	25
		Weak	510	450	500	500		
	P-R Intersections	Strong	480	540	420	435	473	31
		Weak	490	490	455	—		
Mean Deviation from the Means for given Conditions			17	18	30	16		

be chosen for study. The other three are far more serious in an arc than in a low pressure source. In locating maxima, overlapping may be more troublesome than in locating intersections. Inhomogeneity of temperature, which is to be expected only in sources at comparatively high pressure, clearly invalidates any assignment of rotational temperature. Self-absorption and self-reversal would not be expected to change the position of the maximum or the intersections, although these processes result in pronounced deviations from linearity in the intensity factor graphs. The layer of gas between the discharge and the window of the tube in our experiments was at a pressure of about  $10^{-4}$  atmosphere, and about 10 cm long, hence no flattening of line contours was obtained on our plates.

A systematic study of rotational temperatures in comparison with temperatures measured by conventional means has been carried out by Thompson<sup>19</sup> for a low voltage arc in nitrogen, with respect to the negative nitrogen band at 3914A. He found rotational temperatures 300° higher than furnace temperatures of 600°K, and at higher furnace temperatures the discrepancy was less. It is clear from our data that the electrodeless discharge is a much cooler source than

the low voltage arc, since the rotational temperature is within about 90° of the furnace temperatures of 353° and 383°K, and substantially equal to the furnace temperature at about 640°K. Although Thompson estimates the error of the determinations using the intensity factor graphs at 2 percent, his plotted points of differences between rotational and furnace temperatures show fluctuations as high as 20 percent. He offers no explanation for these fluctuations.

A possible use of band lines as calibration marks for photometry of spectrum plates is suggested by the great range of line intensities in a band, and the apparent reproducibility of the intensities under controlled temperature conditions. Our studies are not extensive enough to furnish sufficient evidence on this point, but the distributions obtained so far are remarkably consistent.

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### Band Spectrum of TiCl

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The emission spectrum of TiCl has been excited by both high frequency and low frequency discharges through a continuous flow of TiCl<sub>4</sub> vapor in a discharge tube. The spectrum consists of one strong group of bands and several weaker groups, all degraded to shorter wave-lengths. The strong group occurs between 4200 and 4100A and the weak groups between 4100 and 3700A. The strong group is attributed to a transition between doublet electronic levels. The analysis of this system gives the values  $\nu_e = 23820.0 \text{ cm}^{-1}$ ,  $\omega' = 503.4 \text{ cm}^{-1}$ ,  $x'\omega' = 2.5 \text{ cm}^{-1}$ ,  $\omega'' = 456.4 \text{ cm}^{-1}$ ,  $x''\omega'' = 6.3 \text{ cm}^{-1}$ .

#### INTRODUCTION

FOWLER,<sup>1</sup> in 1907, reported three band heads at 4199.5, 4192.7, and 4188.0A which he at-

tributed to the TiCl molecule. This spectrum has been rephotographed and examined in an attempt to make a vibrational analysis. The spectrum was found to extend from 3700 to 4200A, with the strongest bands between 4150 and

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<sup>1</sup> A. Fowler, Proc. Roy. Soc. A79, 509 (1907).



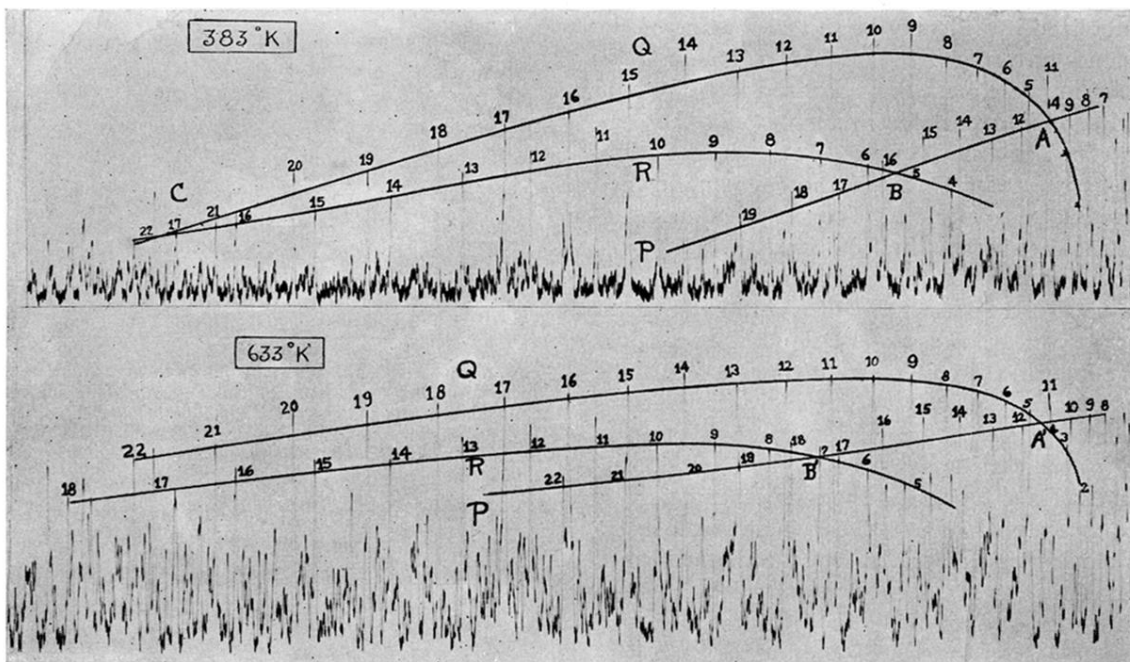


FIG. 4. Microphotometer records of the Angstrom band (0,1)  $\lambda 4835$ , showing  $P$ - $Q$  intersections at  $A, A'$ ;  $P$ - $R$  intersections at  $B, B'$ , and  $Q$ - $R$  intersection at  $C$ . Above, furnace cold; below, furnace hot.  $J''$  values are given for the band lines.