

the specimens were superconducting to the direct current, the resistances to the 60 and 2640 cycle currents were less than could be detected experimentally. Under the best experimental conditions the upper limits of the resistance of the 13-ohm specimen in the superconducting state are  $3 \times 10^{-4}$  and  $2 \times 10^{-3}$  times the resistance just above the threshold temperature for 60 and 2640 cycles respectively.

A current of radio frequency (1,410 kilocycles) was passed through the 13 ohm specimen connected in a tuned circuit loosely coupled to an oscillator. Observation of an electrothermic milliammeter in series with the specimen showed an abrupt increase or decrease in the current as the temperature of the specimen was lowered or raised gradually through the critical or threshold value. The magnitude of the corresponding change in resistance, as inferred from the changes in current produced by resistance changes of known value in the external part of the tuned circuit, was found to be  $0.72 \pm 0.03$  ohm. The excess of this value over the resistance change, 0.13 ohm, observed with direct current is presumably due in part to skin-effect and in part to disturbing effects of the capacitance between the specimen with its leads and the inclosing metal container and conduit. No observable discontinuity in current occurred when the experiment was repeated in an identical way except that the radio-frequency current flowed only in the two leads running to one end of the specimen.

When one of the two specimens carried direct current and the other radio-frequency current, and the temperature in the liquefier was allowed to drift gradually through the critical value, the discontinuity in resistance appeared first in the specimen of low resistance, supplied with direct current, and was followed

a few seconds later by the change in the other specimen. As the "breaks" occurred in the same order for these two specimens on both rising and falling temperature, the lag was presumably, merely the result of the greater thermal insulation of the higher resistance specimen.

In another experiment, a direct current of 6 m.a. was superposed on the radio-frequency current of 36 m.a., and the d.c. potential drop was measured by one observer on the Wenner potentiometer while another watched the electrothermic milliammeter, through which only the radio-frequency current flowed. As the temperature gradually drifted through the critical value, the discontinuity in resistance appeared simultaneously on both instruments.

In a brief note<sup>3</sup> which appeared after these experiments had been carried out, Professor McLennan reports that his earlier experiments had not been crucial and that later work had shown a definite discontinuity in resistance at  $10^7$  cycles per second. He also states that he observed the "break" at a slightly lower temperature for the high frequency current than he did for the direct current. The results reported above may be considered as confirming the first conclusion of Professor McLennan's second article, and as not necessarily conflicting with his second conclusion.

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<sup>3</sup> McLennan, *Trans. Roy. Soc. of Canada* (3rd Series) **25**, 191 (1931).

#### The Spectrum of Carbon Dioxide. II. Electron Levels

In a recent paper in the *Physical Review* I discussed at length the emission spectrum of carbon dioxide in the region between 2800 and 4500 Å. It now appears probable that this spectrum comes from a neutral CO<sub>2</sub> molecule excited to a state about a volt above its ionization potential. This conclusion is based on some very simple experiments of my own and on some new measurements of the absorption spectrum of CO<sub>2</sub> to be published by Henning in the *Zeits. f. Physik* in the near future.

I have been studying the spectrum emitted by the positive column of a Geissler tube discharge in flowing CO<sub>2</sub>, taking simultaneous plates with a fluorite vacuum spectrograph and a medium sized (E2) quartz Hilger spectrograph. My primary object was to complete the search for the Leifson absorption bands in emission. I found no trace of them, thus confirming the results previously obtained with electron beam excitation.

<sup>1</sup> Smyth, *Phys. Rev.* **38**, 2000 (1931).

As so often happens the chief interest of these experiments proved to be in entirely unforeseen results. The plates obtained showed the CO<sub>2</sub> system mentioned above, the fourth positive, third positive, 3A, 5B, Angstrom and probably comet tail systems of CO and a trace of the second positive bands of nitrogen. The first negative bands of CO were certainly not present. The relative intensities of these systems might be expected to depend on the relative concentrations of CO<sub>2</sub> and CO and on the strength of the electrical excitation. These in turn will depend experimentally in a complicated way on the pressure and rate of flow of the gas and on the current in the discharge.

directly from CO<sub>2</sub>, 5.5 volts, the energy required for the dissociation CO<sub>2</sub>→CO+O, must be added giving 15.9 to 16.9 for the positive systems. Duffendack and Smith<sup>2</sup> found that the CO<sub>2</sub> system was excited in mixtures of CO and O<sub>2</sub> with He or Ne but not with A. They explained this in terms of ionic collisions of the second kind but it may be equally well explained in terms of collisions with excited atoms or limited electron velocity and suggests that the excitation potential is between that of argon and neon. A value just below the neon potential (16.6 volts) would be in excellent accord with my results if the CO systems are excited in part or wholly from

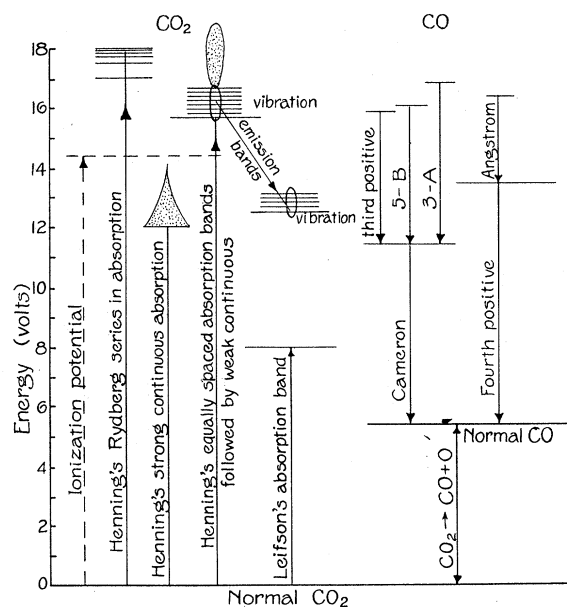


Fig. 1.

Actually I have obtained some twenty-five different exposures under a wide variety of conditions and have observed such variations. The results are only qualitative and an attempt to explain them in detail would be premature. Suffice it to say that they indicate a close relation between the CO systems mentioned above and the CO<sub>2</sub> system, small changes in conditions causing considerable changes in relative intensity. Now the energies required to excite the CO systems from normal CO are from 10.4 to 11.4 volts for the positive systems and 16.6 for the comet-tail bands. If the CO systems can also be excited

CO<sub>2</sub>. Such a value would be above the I.P. of CO<sub>2</sub> (14.4 volts) but this is the only reason for attributing this spectrum to CO<sub>2</sub><sup>+</sup> since it can be excited directly from neutral CO<sub>2</sub> either in the positive column or by an electron beam at low pressures. But if the excitation potential is below 16.6 volts and the electron transition is of the order of three volts the lower state of these bands is below the I.P. of CO<sub>2</sub>. An attractive way out of this dilemma is revealed by Henning's results.

<sup>2</sup> Duffendack and Smith, Phys. Rev. **34**, 68 (1929).

Studying the region below 900A Henning has found three types of absorption in CO<sub>2</sub>, continuous, a Rydberg series of bands and a series of bands equally spaced at intervals of  $1120 \pm 50 \text{ cm}^{-1}$ . These last bands are eight in number with wave-lengths corresponding to from 15.7 to 16.7 volts. Excepting the one of longest wave-length each band is double with a doublet separation of about  $350 \text{ cm}^{-1}$ . Now the upper levels of the CO<sub>2</sub> emission bands have separations given by  $1135 - 3.7v'$ , ( $v' = 1 \cdot \cdot \cdot 9$ ), are eight to ten in number and have an excitation potential probably a little below 16.7 as we have seen. There is therefore good reason to identify them with the upper levels of Henning's absorption bands. It is true that the scheme of vibration levels I gave in my earlier paper would give triplet levels with a total spread of only  $166 \text{ cm}^{-1}$  but that scheme was admittedly subject to correction (see below). I think that we can conclude with assurance that the two sets of upper levels belong to the same electronic state and are probably identical and that consequently the CO<sub>2</sub> emission bands come from a neutral molecule excited above its I.P.

Proceeding on this assumption it is possible to construct an electron level diagram for CO<sub>2</sub> and compare it with the similar scheme for CO. I have included in the figure below the upper level of Leifson's bands<sup>3</sup> though its location can only be guessed.

With reference to the discrepancy between Henning's doublet separation and the nar-

rower triplet predicted by my analysis I may say that the relative intensities of certain bands within the CO<sub>2</sub> system are not the same in my recent plates as in those taken with electron beam excitation last year and that it seems possible that some rearrangement of the levels may be necessary to explain these variations. But as I have not been able to find any equally simple scheme which fits the wave numbers equally well I prefer not to present a different scheme until further data are available. I feel this the more strongly because the proof that this spectrum comes from the neutral molecule makes the application of Denison's theory more plausible. Attempts to rearrange the levels along the lines of Fermi's recent discussion<sup>4</sup> of the Raman effect have not been successful.

I need hardly say that I am continuing the study of this spectrum. Thanks to the support of the Guggenheim Foundation I am doing so in Professor Franck's Institute where my sojourn has already been profitable as well as pleasant. I am indebted to him, to Dr. Sponer, Mr. Henning and others for making it so.

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Zweites Physikalisches Inst. d. Univ.  
Göttingen,  
December 22, 1931.

<sup>3</sup> Leifson, *Astrophys. J.* **63**, 73 (1926).

<sup>4</sup> Fermi, *Zeits. f. Physik* **71**, 250 (1931).

#### Some Studies of Negative Point Discharges at Low Pressures

Only a few spectrographic investigations of point discharges at low pressures have been published.<sup>1</sup> Therefore, the results of some experiments may be of interest which were undertaken to find the lowest pressures at which negative point discharges may be maintained and to study their spectrum emitted in the vacuum.

The main difficulty encountered with point discharges is that a discharge from a pointed conductor is well defined for a very short time only as then the shape of the point will change and accordingly the characteristics of the discharge. For this reason, a wire was taken as cathode; the discharge takes place then only from distinct points which are assumed to be caused by submicroscopic summits on the surface of the wire. The tube used for the investigations was evacuated to a pressure of about

$10^{-3}$  mm Hg. If now a rectified voltage was applied, from one to three bright *light brushes of blue color* appeared starting near the cathode wire. With the pressure decreasing to about  $10^{-4}$  mm Hg the brushes became shorter and finally only bright *blue points* were observed on the wire. The voltage necessary to excite now the point discharges was  $78 \text{ kv}_{\text{max}}$ , the current passing through the tube being  $10^{-4}$  amp. If the pressure was lowered to  $< 10^{-5}$  mm Hg it was not possible to excite the appearance of the blue points with voltages up to  $95 \text{ kv}_{\text{max}}$ .

The point discharges were not affected if the cathode wire was slowly *heated*, at a high temperature, however, the points could visually not be detected. Together with the excitation of the point discharges a considerable *sputtering* from the cathode wire took place,