THE RATE OF THERMAL DIFFUSION
IN MIXTURES OF
CARBON DIOXIDE AND HYDROGEN

Thesis by

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SUMMARY

An equation is derived for the time rate of change of composition of a binary gas mixture of initially uniform composition by thermal diffusion in an apparatus consisting of two chambers, one above the other, connected by a straight tube. The upper chamber is held at a given constant high temperature and the lower chamber at a given constant lower temperature.

Using the thermal conductivity method of analysis the rate of change of composition in the lower chamber has been measured for carbon dioxide-hydrogen mixtures for various compositions, pressures and higher temperatures.

From the experimental results and the derived equation, values are determined for the thermal diffusion coefficient, the ordinary or concentration diffusion coefficient and the temperature exponent for these coefficients.

Acknowledgment is due Professor R. G. Dickinson for suggesting the problem discussed in this thesis and for his direction of the work.

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Thermal Diffusion Rate Curves for CO - H Mixtures:

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A composition gradient will be developed by thermal diffusion in a gas mixture, of initially uniform composition, when it is subjected to a temperature gradient. For a one-dimensional temperature gradient and for constant pressure, Chapman's (1) general diffusion equation for a binary mixture reduces to

$$\underline{v}_1 - \underline{v}_2 = - \frac{1}{F_1 F_2} D_c \left[\frac{\partial F_1}{\partial z} + k_T \frac{1}{T} \frac{\partial T}{\partial z} \right] \quad (1)$$

$\underline{v}_1$ = average velocity of molecules of component 1.

$\underline{v}_2$ " " " " " " " " " " 2.

F_1 = mol fraction of component 1.

F_2 = " " " " " " 2.

D_c = coefficient of ordinary or concentration diffusion.

D_T = " " " " thermal diffusion.

k_T = D_T/D_c = thermal diffusion ratio.

z = coordinate in the direction of the temperature gradient.

T = temperature

Differential Equation for Thermal Diffusion in a Gas Layer

For a layer of gas confined between two parallel surfaces each held at constant but different temperatures, Equation (1) becomes

$$N F_1 \underline{v}_1 = -N D_c \left[\frac{\partial F_1}{\partial z} + \frac{k_T}{T} \frac{\partial T}{\partial z} \right] \qquad (2)$$

N = total number of molecules per unit volume at any given point in the layer.

Equation (2) follows from Equation (1) by the assumption that the thermal conductivity of the gas mixture is not changed by small changes in composition. Then the temperature gradient does not change with time and consequently N also is independent of time. Hence

$$N F_1 \underline{v}_1 = -N F_2 \underline{v}_2 \qquad (3)$$

Also

$$F_2 = 1 - F_1 \qquad (4)$$

Equations (3) and (4) substituted in Equation (1) yield Equation (2).

Equation (2) gives the flux of molecules of kind 1 across the layer.

At any given point in the gas layer the mol fraction F_1 of component 1 changes with time. At time t the number of molecules of kind 1 in a given element of volume at height z (above the cold surface) is

$$N F_1 \, dx \, dy \, dz \; (\text{at } t, z)$$

At time t+dt the number is

$$N F_1 \, dx \, dy \, dz \, (\text{at } t+dt, z)$$

$$= N F_1 \, dx \, dy \, dz \, (\text{at } t, z) + dx \, dy \, dz \, \frac{\partial (N F_1)}{\partial t} \, dt \tag{5}$$

Also the number of molecules in dx dy dz at time t+dt is equal to the number in the given element at the time t plus the number flowing in at the lower surface minus the number flowing out at the upper surface in the time dt. Then

$$N F_1 \, dx \, dy \, dz \, (\text{at } t+dt, z)$$

$$= N F_1 \, dx \, dy \, dz \, (\text{at } t, z) + N F_1 \underline{v}_1 \, dt \, dx \, dy$$

$$- \left[N F_1 \underline{v}_1 + \frac{\partial}{\partial z} (N F_1 \underline{v}_1) dz \right] dt \, dx \, dy \tag{6}$$

Equating (5) and (6)

$$\frac{\partial (N F_1)}{\partial t} = - \frac{\partial}{\partial z} (N F_1 \underline{v}_1) \tag{7}$$

Combining Equations (7) and (2)

$$\frac{\partial (N F_1)}{\partial t} = \frac{\partial}{\partial z} \left\{ N D_c \left[\frac{\partial F_1}{\partial z} + \frac{k_T}{T} \frac{\partial T}{\partial z} \right] \right\} \tag{8}$$

Equation (8) is the partial differential equation applicable to the thermal diffusion process taking place in a layer of gas confined between two parallel surfaces and through which a temperature gradient is maintained. A solution of this equation is given in the appendix.

The Problem of the Two Connected Chambers

In order to determine the expression for the rate of change of composition by thermal diffusion in an apparatus consisting of two chambers connected by a tube and containing a binary gas mixture of initial uniform composition with the top chamber held constantly at T_H and the bottom chamber constantly at T_C , it is assumed that a steady state exists at all times in regard to the composition of the gas in the tube and that the compositions of the gases in the two chambers are uniform at all times. By the assumption of the steady state in the tube it is meant that the composition gradient in the tube always corresponds instantly to that required for thermal diffusion between the gases of the compositions existing at any given instant in the two chambers. (The validity of this assumption is examined in the appendix to this report.) The thermal conductivity of the tube material is assumed to be zero with no heat loss from the tube walls. The volume of the connecting tube is assumed to be negligible in comparison with the volumes of the two chambers.

The following nomenclature is used:

t = time, seconds.

V = volume, cc.

N = total number of molecules per cc at temperature T.

τ = flow of molecules of kind 1, molecules per sq.cm. per sec.

Q = heat flow, cal per sq.cm.per sec.

p = pressure.

a = cross sectional area of tube, sq cm.

h = tube length, cm.

Superscripts: o, ∞ refer to time.

Subscripts: 1 refers to the heavier component.

2 refers to the lighter component.

H, C, refer to hot and cold chambers.

o refers to 0°C. and 760 mm pressure.

Equation (7) gives for the steady state in the tube

$$\frac{\partial}{\partial z}(NF_1 \underline{v}_1) = 0$$

Integrating

$$NF_1 \underline{v}_1 = \text{constant} = \tau$$

Equation (2) then gives for the flux of molecules of kind 1

$$\tau = -ND_c\left[\frac{\partial F_1}{\partial z} + \frac{k_T}{T}\frac{\partial T}{\partial z}\right] \qquad (9.)$$

Following Furry, Jones and Onsager (2), the variable z is next eliminated from Equation (9) and the dependence of the resulting coefficient on T established.

From the definition of the thermal conductivity coefficient λ the amount of heat Q flowing through the gas in the tube is

$$Q = \lambda \frac{\partial T}{\partial z} \qquad (10)$$

Since a functional relation between T and z will exist

$$\frac{\partial F}{\partial z} = \frac{\partial F}{\partial T}\frac{\partial T}{\partial z} = \frac{Q}{\lambda}\frac{\partial F}{\partial T} \qquad (11)$$

Substitution of (10) and (11) in (9) gives

$$\tau = -\frac{Q N D_c}{\lambda}\left[\frac{\partial F}{\partial T} + \frac{k_T}{T}\right] \qquad (12)$$

From kinetic theory, assuming specific heat to be constant

$$\begin{aligned} D_c &= D_{oc}\left(\frac{T}{T_0}\right)^{1+s}\frac{P_0}{P} \\ \lambda &= \lambda_0\left(\frac{T}{T_0}\right)^{s} \\ N &= N_0\,\frac{T_0}{T}\,\frac{P}{P_0} \end{aligned} \qquad (12a)$$

Then

$$\frac{N D_c}{\lambda} = \frac{N_0 D_0}{\lambda_0}$$

As stated previously the coefficient of thermal conductivity is assumed not to change with changes of composition. The heat flow through the gas from end to end of the adiabatic tube is constant and a function of the length and cross sectional area of the tube, the end temperature and λ. Q is therefore a constant in Equation (12). Its magnitude is

$$Q(z_H - z_c) = Qh = a\int_{T_c}^{T_H} \frac{\lambda_0}{T_0^{s}} T^{s} dT$$

$$Q = \frac{a}{h} \frac{1}{1+s} \frac{\lambda_0}{T_0^{s}} \left(T_H^{1+s} - T_c^{1+s} \right)$$

Let

$$B = \frac{Q N_0 D_{0c}}{\lambda_0} = \frac{1}{1+s} \frac{a}{h} \left(T_H^{1+s} - T_c^{1+s} \right) \frac{N_0 D_{0c}}{T_0^{s}} \qquad (13)$$

Then Equation (12) becomes

$$\frac{\partial F_1}{\partial T} = -\frac{\tau}{B} - \frac{k_T}{T} \qquad (14)$$

The thermal diffusion ratio is practically constant with respect to pressure and temperature. (As shown by experimental data given later, See also references 3, 4, and 5.) Its value is a function of the composition of the mixture, but for small changes in composition it may be assumed to be constant without serious error.

Integrating Equation (14) and substituting limits, the flux of molecules of kind 1 through the tube is

$$\tau = \frac{-B}{T_H - T_c}\left[(F_{1H} - F_{1c}) + k_T \ln T_H/T_c\right] \qquad (15)$$

Since the total number of molecules of kind 1 in the system remains constant, then, neglecting the volume of the connecting tube

$$N_c F_{1c} V_c + N_H F_{1H} V_H = F_1^{\circ}(N_c V_c + N_H V_H) \qquad (16)$$

With $N_c/N_H = T_H/T_c$ there results the equation

$$F_{1H} - F_{1c} = (F_1^{\circ} - F_{1c})\left(\frac{T_H V_c}{T_c V_H} + 1\right) \qquad (17)$$

Let

$$b = \frac{T_H V_c}{T_c V_H} + 1 \qquad (18)$$

Substituting (17) in (15)

$$\tau = -\frac{B}{T_H - T_c}\left[b(F_1^{\circ} - F_{1c}) + k_T \ln T_H/T_c\right] \qquad (19)$$

τ represents a steady flow of molecules through the tube from the cold chamber to the hot chamber at any given time but changes instantaneously with the slow change of the concentrations in the two chambers.

The change in the number of molecules of kind 1 in the cold chamber with time is equal to the rate of flow of kind 1 into the chamber.

$$N_c V_c \frac{dF_{1c}}{dt} = -\tau = \frac{B}{T_H - T_c}\left[b(F_1^\circ - F_{1c}) + k_T \ln T_H/T_c\right]$$

$$\frac{dF_{1c}}{dt} + \frac{Bb}{N_c V_c (T_H - T_c} F_{1c} = \frac{B}{T_H - T_c}\left[b\, F_1^\circ + k_T \ln T_H/T_c\right]$$

Integrating

$$F_{1c} - F_1^\circ = \frac{k_T}{b} \ln \frac{T_H}{T_c} + c'' e^{\frac{-Bb}{N_c V_c (T_H - T_c)} t}$$

At time t = 0

$$F_{1c} = F_1^\circ$$

$$c'' = -\frac{k_T}{b} \ln T_H/T_c$$

Then

$$F_{1c} - F_1^\circ = \frac{k_T}{b}\left(\ln \frac{T_H}{T_c}\right)\left(1 - e^{\frac{-Bb}{N_c V_c (T_H - T_c)} t}\right) \qquad (20)$$

Substituting the values of B and b, the exponent becomes

$$c = \frac{1}{1+s} \cdot \frac{a}{h} \cdot \frac{T_H^{1+s} - T_c^{1+s}}{T_H - T_c} \cdot \frac{T_c}{T_0^{1+s}} \cdot \frac{D_{0c}}{V_c} \cdot \frac{\rho_0}{\rho}\left[1 + \frac{T_H V_c}{T_c V_H}\right] \qquad (21)$$

Equation (20) is the final expression for the rate of change of the composition of the gas in the cold chamber.

As a check on Equation (20) the steady state condition at time $t = \infty$ may be investigated. For the steady state the flux of molecules of kind 1 is zero. Equation (2) then becomes

$$\frac{\partial F_1}{\partial z} = - \frac{k_T}{T} \frac{\partial T}{\partial z}$$

Integrating and substituting limits

$$F_{1H}^{\infty} - F_{1c}^{\infty} = -k_T \ln T_H/T_c \qquad (22)$$

Using Equation (17)

$$F_{1c}^{\infty} - F_{1c}^{0} = \frac{k_T}{p} \ln T_H/T_c \qquad (23)$$

Equation (20) reduces to Equation (23) at t

Dividing Equation (20) by Equation (23) gives

$$\frac{F_{1c} - F_1^{0}}{F_{1c}^{\infty} - F_{1c}^{0}} = 1 - e^{-ct} \qquad (24)$$

Equation (21) provides a relation for the determination of s and D_{oc} from experimentally determined values of c. Assume experimental values c and c' for temperatures T_H and T_H'

are available, then the expression for s derived from Equation (21) is

$$\frac{c}{c'} \cdot \frac{\rho'}{\rho} \cdot \frac{\left[1 + \frac{T_H' V_c}{T_c V_H'}\right]}{\left[1 + \frac{T_H V_c}{T_c V_H}\right]} \cdot \frac{T_H - T_c}{T_H' - T_c} = \frac{T_H'^{(1+s)} - T_c^{1+s}}{T_H^{1+s} - T_c^{1+s}} \qquad (25)$$

To determine D_{OT} Equation (20) is differentiated with respect to t, giving

$$\frac{\partial F_{1c}}{\partial t} = \frac{k_T}{b} \cdot c \cdot \ln \frac{T_H}{T_c} \cdot e^{-ct}$$

At $t = 0$

$$\left(\frac{\partial F_{1c}}{\partial t}\right)_{t=0} = \frac{k_T}{b} \cdot c \cdot \ln \frac{T_H}{T_c} \qquad (26)$$

By definition

$$k_T = \frac{D_T}{D_c} \qquad (27)$$

Since k_T is taken as independent of pressure and temperature, then D_T is a function of pressure and temperature of the same form as D_c. That is

$$D_T = D_{OT}\left(\frac{T}{T_0}\right)^{1+s} \frac{P_0}{P} \quad \text{and} \quad k_T = \frac{D_{OT}}{D_{OC}} \qquad (28)$$

From Equations (26), (27), (28) and (21)

$$D_{0T} = \left(\frac{\partial F_{1c}}{\partial t}\right)_{t=0} (1+s)\, \frac{h}{a}\, \frac{T_H - T_c}{T_H^{1+s} - T_c^{1+s}} \cdot \frac{T_0^{1+s}}{T_c} \cdot \frac{\rho}{\rho_0} \cdot \frac{V_c}{\ln T_H/T_c} \qquad (29)$$

From an experimentally determined value of s or a value of s from other sources and the experimental value of the initial slope, the thermal diffusion coefficient may be determined.

Values of k_T may be determined from experimental data by use of either Equation (22) or Equation (23). Then with D_{0c} known, the value of D_{0T} results immediately from Equation (27).

Combining Equations (27) and (23) there is obtained the equation

$$D_{0T} = D_{0c} (F_{1c}^{\infty} - F_{1c}^{0}) \left[1 + \frac{T_H V_c}{T_c V_H}\right] \frac{1}{\ln T_H/T_c} \qquad (30)$$

Using Equation (23), Equation (26) becomes

$$\left(\frac{\partial F_{1c}}{\partial t}\right)_{t=0} = (F_{1c}^{\infty} - F_{1c}^{0})\, c \qquad (31)$$

Two other expressions of use in reducing and checking experimental data are as follows:

From Equations (23) and (22)

$$b = 1 + \frac{T_H V_C}{T_C V_H} = \frac{k_T \ln T_H/T_C}{F_{1C}^{\infty} - F_{1C}^{0}} = \frac{F_{1C}^{\infty} - F_{1H}^{\infty}}{F_{1C}^{\infty} - F_{1C}^{0}} \qquad (32)$$

From Equations (20) and (23)

$$\ln\left[\frac{F_{1C}^{\infty} - F_{1C}}{F_{1C}^{\infty} - F_{1C}^{0}}\right] = ct \qquad (33)$$

Experimental Apparatus

A two-chamber apparatus was constructed as shown in cross section by Fig. 1. This consists of a pyrex glass hot chamber and a brass cold chamber connected by a pyrex glass tube. The hot chamber is provided with a thermocouple well and is surrounded by an electric furnace. The cold chamber contains a valve stem and disc, for closing off the connecting tube, and a stirrer. The stirrer drive shaft is brought out through a hardened steel lapped journal and bearing and provided with an oil-seal filled with vacuum pump oil. The cold chamber also contains a thermal conductivity cell for following the changes in composition of the CO_2- H_2 mixtures. The hot and cold chambers are provided with 1 mm inside diameter capillary connections for gas flow. The pyrex connecting tube is cemented into the brass flange which is bolted to the cold chamber. The gaskets in the cold chamber are either koroseal or neoprene except the valve stem packing which is graphited asbestos cord. Further dimensional data are given later.

The wiring diagram and gas connections are shown in Fig. 2. The cold chamber is immersed in a thermostatically controlled water bath up to the brass flange of the connecting tube as indicated. The vacuum manometer and the two aspirators shown are mercury-filled. The first aspirator is for transferring the gas from either the cold or hot chamber to the second aspirator from which portions are then withdrawn for analysis in a Burrell precision type gas analysis apparatus, the CO_2 being absorbed in $NaOH$ solution.

The wiring diagram for the thermal conductivity cell follows the detailed discussion of this method of analysis given by Palmer and Weaver (6). The current through the circuit is standardized by adjusting a rheostat to obtain a balance across the first bridge circuit, the resistances in this circuit having been selected to give the desired current of about 0.4 ampere. The current control cell consists of a 4-inch length of platinum wire of .0035-inch diameter stretched along the center of a 4-inch length of ½-inch outside diameter by 3/8-inch inside diameter copper tubing. Glass caps cemented to the ends of the tube serve to seal in an atmosphere of air and to electrically insulate and support the platinum wire. This cell is immersed in the water bath. The high temperature coefficient of resistance of the platinum wire provides the means for sensitive current adjustment. The two 10 ohm resistances in this bridge were "Ohmite" and the third made of manganin wire. No. 18 ga. insulated copper was used for general wiring.

The conductivity bridge circuit consists of two 10 ohm manganin resistances, a comparison cell similar to the current control cell, also placed in the water bath, and the conductivity cell in the cold chamber. A continuous slow stream of dry hydrogen is circulated through the comparison cell and out through a bubbling bottle. The conductivity cell in the cold chamber consists of a 4-inch length of platinum wire of about .002 inch diameter stretched along the center of a 4-inch length of 1/2 inch outside diameter by 3/8 inch inside diameter copper tube which in turn is soldered in a recess in the inside wall of the cold chamber as shown in Fig. 1. The electrically insulating gas-tight joints for the conductivity cell consist of short lengths of koroseal rubber tubing compressed between bakelite sleeves as shown in Fig. 1, which follows substantially the construction of the Shakespeare thermal conductivity unit described by Palmer and Weaver. Potentials were measured by a Leeds and Northrup type K potentiometer.

No. 30 ga. chromel-alumel thermocouples were placed in the well in the hot chamber and at the upper and lower ends of the furnace as shown in Fig. 1.

Experimental Procedure

Following is the finally established experimental procedure:

A CO_2-H_2 mixture of the desired composition is first made up using cylinder gases dried by passing through activated alumina and the mixture stored in a small steel cylinder for 12 to 24 hours before use. With constant furnace and water bath temperatures established and maintained over a period of several hours and with the connecting tube valve in the cold chamber closed, the hot and cold chambers are evacuated to 2 mm Hg or less, then charged to 500 mm with the gas mixture, the chambers again evacuated and finally charged to a pressure about 10 mm Hg below the desired running pressure. The feed lines to the hot and cold chambers are then shut off and the potential drop across the conductivity bridge determined for the given pressure. More gas mixture is then admitted only to the cold chamber until its pressure is about 10 mm Hg above the desired running pressure and the potential again determined. Before each potential reading, the standard cell current and the bridge current are checked.

The connecting tube valve is then opened and the time noted. Readings of potential, time and bath temperature are then taken as frequently as possible at the start of an experiment. Then later, thermocouple readings and cold chamber pressures are taken at intervals.

After the conductivity bridge potential has attained a constant value over a period of at least an hour the connecting tube valve is closed.

At the time of charging the apparatus a 200 cc sample of the original mixture is drawn into the first aspirator chamber. Three to five analyses of this sample are now made using 30 cc portions. The aspirator chambers and the manifold are now evacuated. The major portion of the gas in the hot chamber is then transferred to the second aspirator chamber and analyzed, using 20 to 30 cc samples, depending on the amount available to permit at least three analyses. The same procedure is then followed for the gas in the cold chamber.

Calibrations and Preliminary Observations

The current control bridge was found to be very sensitive and reliable. It was found necessary to place a 0.2 ohm slide-wire rheostat in series with the main control rheostat to make use of the available sensitivity.

A calibration curve for the thermal conductivity unit showing percent CO_2 vs. millivolts drop across the bridge is shown in Fig. 3. This curve is made up from the results of analyses made for later experiements. It was originally intended to determine such a calibration curve at the start of the investigation and use it for the determination of all gas compositions. However, it was found that the base point of the conductivity unit varied for some unascertained reason from day to day by as much as .4 mv. This variation is shown by the insert curves at the top of Fig. 3, showing the millivolt readings plotted against the percent CO_2 as determined by absorption in NaOH for experiments No. 7, 10, 15 and 18, being those made on 30% CO_2 mixture at 760 mm pressure. The variation of about ± 0.15 millivolt, as shown by these curves, corresponds to ± 0.2% variation in CO_2 content. Since the absorption method of analysis was believed to give greater accuracy than this, it was chosen as the standard for determination of gas composition and the thermal conductivity method used to determine the rate of change of composition. A straight line relation was used to convert change in conductivity bridge potential to change in percent CO_2. Over the range of composition of 4% CO_2 involved, the maximum deviation of the main curve of Fig. 3. at 30% CO_2 from a straight line is about 0.02%.

The potential drop across the bridge was very sensitive to changes in current through the bridge and to changes in bath temperature. A change of 1 milli-ampere in a total current of 360 milli-amperes causes a change of about 0.2 millivolt in the potential drop. (A change of 3% in the CO_2 content of 30% CO_2 mixture results in a total of 2.5 millivolts change in potential.) A 0.1° C. increase in bath temperature causes a 0.2 millivolt drop in bridge potential. This results no doubt from the fact that the current control and comparison cells follow the bath temperature more quickly than the conductivity cell inside of the cold chamber. Consequently, efforts were made to hold the bath temperature within a range of $\pm 0.01°$ C.

The buret of the gas analysis apparatus was calibrated at 5 cc intervals, using mercury. The pressure balancing chamber in the Burrell apparatus was reduced in size to about 40 cc so that it would be subject to the same range of water jacket temperature as the 30 cc sample in the buret. A stream of hydrogen was bubbled through the back chamber of the NaOH pipette to keep the solution saturated with hydrogen, since the residual gas after CO_2 absorption is hydrogen.

The furnace for heating the hot chamber was made by winding 90 turns of No. 20 ga. chromel wire on a 3-inch inside diameter by 3-1/4-inch outside diameter copper tube

12 inches long. A layer of thin mica plus one layer of 1/16-inch thick asbestos paper was applied to the tube before winding. Transite end plates and end ~~end~~ plugs were made as shown in Fig. 1. Insulation around the winding was 1-1/4-inch magnesia. The winding was provided with a center tap, thus making two coils in parallel. Voltage control was by means of an auto transformer. The furnace required a total of 4.6 amperes a.c. at 62 volts to maintain a temperature of 450° C. and 3.7 amperes at 48 volts for 330° C.

The temperature as measured inside of the top head of the furnace is 8° C. lower than that measured in the thermometer well of the hot chamber. The temperature just above the lower head of the furnace near the copper tube is 16° C. lower than the hot chamber temperature. These differences apply for a 450° C. hot chamber temperature. For 330° C. these differences are 5° and 13°.

One of the chromel-alumel thermocouples was compared with a previously standardized Pt.-10% Pt. Rh. thermocouple by inserting the two couples together in a single horizontal thermometer well about 8 inches deep in the center of a 1-inch diameter horizontal furnace, 11 inches deep. The maximum variation of the chromel-alumel couple from the manufacturer's table of millivolt equivalents was 0.02 millivolt or 0.5° C. for temperatures up to 430° C.

The volumes of the cold and hot chambers were determined by weighing empty and filled with water. The cold chamber, made of brass, has an outside length of 7-1/2 inches, outside diameter of 3 inches, inside length of 5 inches and inside diameter of 1-11/16 inches. Its net volume, with connecting tube valve closed, is 179.8 cc at 30° C. With valve open, the net volume is 181.0 cc.

For Experiments No. 4, 5, 7, 8, and 9, the hot chamber was 2-1/2 inches in diameter and 7 inches long, with a volume at 450° C. of 468 cc (not including the volume of the connecting tube). The average diameter of the connecting tube, as determined by the weight of mercury held by a given length of the tube, was 1.312 cm. The tube length, including the brass connecting flange, was 19.05 cm. The tube volume was 25.7 cc.

For Experiments Nos. 10 to 20, inclusive, the hot chamber volume at 450° C is 452 cc. The connecting tube diameter is 0.805 cm and the length, 15.87 cm. The tube volume is 8.1 cc. (Efforts were made to use shorter connecting tubes, but they required reducing the thickness of the lower insulating head to such an extent that the inequality in furnace temperature was increased to around 50°C.)

Experiments No. 4 and No. 5 were run to determine the value of the stirrer in the cold chamber. For No. 4

a 49.5% CO_2-50.5% H_2 mixture was used with the stirrer not operating. For Experiment No. 5 the same gas was used after remixing by means of the mercury aspirator. The successive millivolt readings for the two experiments are shown in Fig. 4. The initial potential before opening the valve for Experiment No. 5 was 0.11 millivolts higher than for No. 4. On the basis of the results shown in Fig. 4 the stirrer was not used in the experiments following No. 5.

In Fig. 4 it will be noted that the curves drawn through the experimental points do not intersect the zero time axis at the initial millivolt readings. It was later realized that this was due to the relatively instantaneous attainment of the thermal diffusion steady state in the connecting tube (see appendix A) increasing the CO_2 content in the lower end of the tube to 56% CO_2 (for a 49.5% CO_2 mixture) so that a concentration diffusion in addition to the thermal diffusion occurs for a short time immediately after the connecting tube valve is opened. This difficulty was partly overcome by starting an experiment with the cold chamber pressure somewhat higher than the hot chamber pressure so that a certain amount of gas swept up through the connecting tube upon opening of the connecting tube valve. The amount of gas swept up through the tube was first selected to be equal to three times the connecting tube volume. This was later reduced to one-half of the connecting tube volume. A time correction, first determined graphically and later corrected, if necessary, to obtain a constant value for the exponent in the rate expression, was applied to each experiment.

Data from Experiments

Twenty experiments in all were run, of which the results from the first six were discarded. The pertinent data are given in Table I, covering Experiments Nos. 7 to 20, inclusive. The experimentally determined values for the CO_2 content in the cold chamber, at various times after the opening of the connecting tube valve, minus the CO_2 content in the initial mixture, are plotted as points in Figures 5 to 9, inclusive. The curves drawn in these figures are calculated by Equation (20), using the finally selected values of the exponent c to give the best fit in each case. The values of c, the time corrections used and the values of the initial slopes, are given in Table II.

All experiments were run with a cold chamber temperature of 30.0° C., or 303° K.

The gas analyses in Table I are given to four significant figures. While in most cases these are the averages of three to five fairly consistent values, there were enough disagreeing values obtained to cast doubt on the ultimate accuracy of the gas analysis method and apparatus. The best that can be said for these values is that they are probably good to the nearest tenth percent.

TABLE I

Ex. No.	Pres. after opening Tube Valve mm Hg	Temp. of Hot Chamber °C.	Conductivity Bridge Potential Millivolts		Total Change of Pot. Millivolts	Gas Analyses Percent CO_2			Change of CO Content in Cold Chamber		$b = 1 + \frac{T_H V_C}{T_C V_H}$	$b = \frac{F_{1C}^{\infty} - F_{1H}^{\infty}}{F_{1C}^{\infty} - F_{1C}^{0}}$
			Avg. Init.	Final		Initial Mixture	Final Cold Chamber	Final Hot Chamber	%	$\frac{\%}{\text{Mv.}}$		
7	757	720	21.48	23.88	2.40	30.72	34.06		3.34	1.39		
8	302	"	22.05	24.50	2.45	"	34.14		3.42	1.40		
9	505	"	21.66	24.16	2.50	"	34.14		3.42	1.37		
10	765	732	20.63	23.11	2.48	29.26	32.86	25.62	3.60	1.45	1.97	2.01
11	302	"	21.16	23.68	2.52	"	32.84	25.79	3.58	1.42	1.97	1.97
12	501	"	21.09	23.54	2.45	29.44	33.10	25.84	3.66	1.49	1.97	1.98
13	299	601	21.71	23.76	2.05	29.90	32.90	27.29	3.00	1.46	1.80	1.87
14	509	"	21.24	23.38	2.14	29.90	33.01	27.29	3.11	1.45	1.80	1.84
15	760	"	21.14	23.31	2.17	30.20	33.31	27.75	3.11	1.43	1.80	1.79
16	300	720	22.24	24.64	2.40	30.10	33.58	26.57	3.48	1.45	1.95	2.01
17	512	"	21.45	23.98	2.53	30.10	33.61	26.57	3.51	1.39	1.95	2.01
18	760	"	21.31	23.83	2.52	30.10	33.56	26.52	3.46	1.37	1.95	2.04
19	761	720	36.83	40.63	3.80	49.85	53.45	46.31	3.60	0.95	1.95	1.98
20	760	"	60.45	64.92	4.47	68.98	71.78	66.53	2.80	0.63	1.95	1.88

Experiments Nos. 7- 9, Inclusive, Connecting Tube Diameter 1.312 cm Length 19.05 cm
" " 10-20, " " " " 0.805 " " 15.87 "

TABLE II

Ex. No.	Initial Pressure Mm Hg Absolute		Pressure After Opening Connecting Tube Valve	Time Correction Minutes	Rate Coef. c	Initial Slope
	Cold Chamber	Hot Chamber				
7	757	757	757	+ 1.3	0.00058	0.0000194
8	302	302	302	+ 0.8	.00150	.0000512
9	505	505	505	+ 1.25	.00090	.0000308
10	865	665	765	- 1.5	0.00029	0.0000104
11	352	252	302	0.0	.00068	.0000243
12	565	432	501	- 0.8	.00043	.0000156
13	315	287	299	- 1.0	0.00058	.0000174
14	521	500	509	0.0	.00038	.0000119
15	777	746	760	0.0	.00025	.0000078
16	310	291	300	0.0	0.00066	.0000230
17	523	502	512	- 1.0	.00044	.0000155
18	773	747	760	0.0	.00029	.0000100
19	773	750	761	- 0.4	0.000266	.0000096
20	772	751	760	+ 0.6	.000256	.0000069

Calculated Results

According to Equation (21) the exponent c should be inversely proportional to the pressure and directly proportional to the value of a/h, that is, connecting tube area divided by length.

The results in Table III show that the exponent follows the pressure dependence fairly well from 760 mm to 500 mm, but for the range extended to 300 mm the deviation approaches 10%. The dependence on tube dimensions is shown in Table IV. These variations, of course, include the experimental errors.

Using Equation (25), values for $1+s$ and D_{oc} may be calculated from six pairs of values of c from Experiments Nos. 10 to 18, inclusive. Of these, four pairs give values for $1+s$ within the kinetic theory limits of 1.5 to 2.0. The values are as follows:

Experiment Numbers	Pressure mm	$1+s$	D_{oc}
11 and 13	300	1.59	0.48
17 and 14	500	1.58	0.54
10 and 15	760	1.50	0.55
18 and 15	760	1.55	0.54
	Average	1.55	0.54 (last 3 values)

The value of $1+s$ for CO_2 - H_2 mixtures, given in the International Critical Tables, is 1.75, and of D_{oc} it is 0.55.

The values for D_{oT} have been calculated using $1+s = 1.55$ in Equation (29) and the results given in Table V. Also in this table are the values of k_T calculated by Equation (22)

TABLE III

Ex. 1	Ex. 2	p_1	p_2	$\frac{p_1}{p_2}$	$\frac{c_2}{c_1}$	Percent Variation
7	8	757	302	2.51	2.58	+2.8
7	9	757	512	1.50	1.55	+3.3
9	8	512	302	1.67	1.67	0.0
10	11	765	302	2.53	2.34	-7.5
10	12	765	501	1.53	1.48	-3.4
12	11	501	312	1.66	1.58	-5.0
15	13	760	299	2.54	2.32	-8.7
15	14	760	509	1.49	1.52	+2.0
14	13	509	299	1.70	1.53	-9.9
18	16	760	300	2.53	2.28	-9.7
18	17	760	512	1.49	1.52	+2.0
17	16	512	300	1.71	1.50	-12.2

TABLE IV

Ex. 1	Ex. 2	p_1	p_2	$\frac{\left(\frac{a}{h}\right)_1}{\left(\frac{a}{h}\right)_2}$	$\frac{c_1}{c_2}\,\frac{p_2}{p_1}$	Percent Variation
7	18	757	760	2.21	2.01	- 9.0
9	17	505	512	2.21	2.08	- 6.0
8	16	302	300	2.21	2.26	+ 2.3

TABLE V

Ex. No.	Initial Mixture % CO_2	Pressure mm Hg	D_{oT} by Eq.(29)	D_{oT} by Eq.(27) $D_{oc} = 0.54$	k_T Eq.(22)	k_T Eq.(23)
7	30.7	757	.037			.074
10	29.3	765	.043	.044	.082	.080
15	30.2	760	.044	.044	.081	.082
18	30.1	760	.042	.044	.081	.078
19	49.9	761	.040	.044	.082	.081
20	69.0	760	.029	.033	.061	.063
9	30.7	505	.039			.075
12	29.4	501	.042	.044	.082	.082
14	29.9	509	.045	.045	.083	.082
17	30.1	512	.044	.044	.081	.079
8	30.7	302	.038			.075
11	29.3	302	.040	.043	.080	.080
13	29.9	299	.039	.044	.082	.079
16	30.1	300	.038	.044	.081	.078

and by Equation (23). Using the values of k_T from Equation (23) and $D_{oc} = 0.54$, the values of D_{oT} are calculated by Equation (27) and given in the table. A comparison of the values of k_T with other values taken from the literature is made in Figure 10.

Discussion of Results

The thermal diffusion coefficient given in Table V for Experiment No. 20 is much lower than that for Experiment No. 19, yet the experimentally found coefficients for the rate equation are nearly the same for the two experiments. This may be clarified somewhat by a further examination of Equation (19) giving the rate of transport of constituent 1, in this case CO_2, through the connecting tube. Equation (19) may be rewritten using Equations (13) and (27)

$$\tau = \frac{-1}{1+s} \frac{a}{h} \frac{T_H^{1+s} - T_C^{1+s}}{T_0^s (T_H - T_C)} \cdot N_0 \left[D_{oc}\, b(F_{1c}^0 - F_{1c}) + D_{oT} \ln \frac{T_H}{T_C} \right] \qquad (34)$$

The second term on the right gives the transport of CO_2 down the tube due to the thermal diffusion and the first term the counter transport of CO_2 up the tube by concentration diffusion. According to this equation the rate of transport by thermal diffusion alone is not a function of the change of concentration of CO_2 in the two connected chambers and therefore does not change from the beginning to the end of a thermal diffusion process. Exception to this must be taken, of course, in so far as k_T and therefore D_{oT} changes with change of concentration. (The change of k_T is a matter of 10% or so for a 3% separation in the cold chamber for 70% CO_2 mixture. For the range of mixtures from 30% CO_2 to 60% CO_2 the change is much less.) With a constant thermal diffusion rate the net separation in the final steady state when the thermal diffusion rate and concentration diffusion rate are equal and opposite is determined only by the thermal diffusion rate. With a direct proportionality existing between the rate of thermal diffusion and the final net separation, as given by Equation (30), the time for thermal diffusion alone to occur in mixtures of a given pair of gases under given pressure and temperature conditions is constant for all concentrations. The time required for a given fraction of the separation to take place in the actual combined thermal and concentration diffusion processes is therefore a function only of the concentration diffusion process. Since the concentration diffusion coefficient is relatively constant for changes in the proportions of a binary gas mixture (the extreme variation being "decidedly" less than 13% according to Chapman (1)) the time required for the actual thermal diffusion process should be independent of concentration. This is the result indicated by the previously given Equation (24). The half life periods for Experiments

Nos. 18, 19 and 20, covering a range of concentration, are as follows:

Experiment Number	Initial % CO_2	Half Life Minutes
18	30.1	39.8
19	49.8	43.4
20	69.0	45.2

If D_{oc} is constant then from Equation (30)

$$\frac{F_{1c}^{\infty} - F_{1c}^{o}}{D_{OT}} = constant \tag{35}$$

The values of this ratio calculated by using the values for $F_{1c}^{\infty} - F_{1c}^{o}$ from Table I and the values of D_{OT} from Table V, determined by use of the initial slopes of the rate curves, are as follows:

Experiment Number	Initial % CO_2	Ratio
18	30.1	0.82
19	49.8	0.90
20	69.0	0.96

From these results the ratio is constant only to the order of plus or minus 10% of the average value.

Comparison of Experimental and Calculated Values of the Exponent c in the Rate Equation

Table VI contains values of 1 + s calculated by Equation (21), using the experimental values of the coefficient c and with $D_{oc} = 0.54$. It also contains the values of c calculated by

TABLE VI

Ex. No.	Initial % CO_2	p mm Hg	T_N °K	$\frac{h}{a}$	Time Cor. Used in Determining Expt. Value of c	Expt. c	1 + s Calc. From Expt. Value of c and D_{oc} = 0.54	Calc. c For D_{oc}=0.54 and 1 + s = 1.75	$\frac{c\ Calc}{c\ Expt}$
7	30.7	757	720	14.09	+ 1.3	.00058	1.38	.000731	1.26
10	29.3	765	732	31.18	− 1.5	.00029	1.53	.000334	1.15
15	30.2	760	601	"	0.0	.00025	1.55	.000278	1.11
18	30.1	760	720	"	0.0	.00029	1.55	.000329	1.13
19	49.9	761	720	"	− 0.4	.000266	1.39	.000329	1.24
20	69.0	760	720	"	+ 0.6	.000256	1.35	.000329	1.28
9	30.7	505	720	14.09	+ 0.8	.00090	1.37	.00110	1.22
12	29.4	501	732	31.18	− 0.8	.00043	1.49	.000508	1.18
14	29.9	509	601	"	0.0	.00038	1.58	.000414	1.09
17	30.1	512	720	"	− 1.0	.00044	1.58	.000489	1.11
8	30.7	302	720	14.09	+ 1.25	.00150	1.43	.00183	1.22
11	29.3	302	732	31.18	0.0	.00068	1.41	.000845	1.24
13	29.9	299	601	"	− 1.0	.00058	1.37	.000705	1.22
16	30.1	300	720	"	0.0	.00066	1.38	.000835	1.26

Equation (21) using $1 + s = 1.75$ and $D_{oc} = 0.54$ and the ratios of these calculated values to the experimental values.

Nine out of the fourteen calculated values of $1 + s$ are below the lower limit of 1.5 furnished by kinetic theory for elastic spheres, indicating that the experimental values of c are too low. Low values of the coefficient c could result from the actual thermal diffusion rate being slower than that called for by Equation (20), by a lag in the experimental method used in determining the rate, or by error in the determination of the temperature of the hot chamber. The effect of possible error in the temperature measurement may be disregarded immediately, since a drop of 30° C. in temperature of the hot chamber reduces the calculated value of the coefficient c by only 2%. If there were a serious lag in the thermal conductivity cell it is believed this lag would show up by a sagging of the experimental points below the exponential curves during the early part of an experiment in an amount proportional to the rate of thermal diffusion. Since the experimental points follow the exponential curves quite well in all cases it is believed there is no serious lag in the experimental method.

If the twelve experiments run on the 30% CO_2 mixture are arranged in the order of the value of the exponent there is a downward tendency in the ratio of the calculated to experimental values of the exponent as shown by the following tabulation:

Experiment Number	Experimental Value of c	$\frac{\text{Calc. Value of c}}{\text{Expt. Value of c}}$
8	0.00150	1.22
9	.00090	1.22
11	.00068	1.24
16	.00066	1.26
7	.00058	1.26
13	.00058	1.22
17	.00044	1.11
12	.00043	1.18
14	.00038	1.09
10	.00029	1.15
18	.00029	1.13
15	.00025	1.11

This would indicate, as might be expected, that the theoretical rates are attained only at very slow rates, that is, for large values of the ratio of length to cross sectional area of the connecting tube. However, this conclusion is not supported by Experiments Nos. 19 and 20 for the mixtures richer in CO_2 which have values of c lower than any of the above and yet show high ratios of calculated to experimental values of c.

Application of Equation (20) to the Data of Schmahl and Schewe

Experimental data on the rate of thermal diffusion at 300 mm pressure in one mixture of CH_4 and H_2 and one mixture of CO_2 and CO are given by Schmahl and Schewe(4) They used a two-chamber glass apparatus in which the diameter of both chambers was 2 cm. The length of the hot chamber was 21 cm and of the cold chamber 7 cm. The connecting tube, containing a stop-cock, was 0.5 cm inside diameter and 12 cm long. The value of connecting tube length divided by cross sectional area is 61.2 for the apparatus. The higher temperature was 500°C and the lower temperature 21° C. For each gas mixture a series of tests were run, each for a definite period of time, after which the connecting tube stopcock was closed and the gases in the two chambers analyzed.

The data are shown in Figures 10 and 11. The curves drawn for the $CH_4 - H_2$ mixture were calculated using $D_{oc} = 0.625$ and for the $CO_2 - CO$ mixture $D_{oc} = 0.137$, as given by the International Critical Tables. The data are not sufficiently consistent to permit any evaluation of the exponent $1 + s$. However, use of the value of $1 + s = 1.75$, as given by the International Critical Tables, would give rate curves that are in fairly close agreement with the experimental data.

The results of Schmahl and Schewe are included here since they show the wide range of values of D_{oc} over which the use of Equation (20) gives reasonable rate curves and also because they indicate that for the larger ratios of connecting tube length to cross sectional area the actual rate of thermal diffusion may be expected to agree with that given by Equation (20).

Comments on the Design and Operating Characteristics of the Apparatus

In their discussion of the thermal conductivity method of gas analysis, Palmer and Weaver (6) state that the thermal conductivity cell and the comparison cell should be placed in the same metal block to insure both cells being at the same temperature. This procedure was not followed because of the complexity thus involved in the design of the cold chamber, it being assumed that sufficiently close control of the water bath temperature could be obtained to keep the two chambers always at the same temperature. However, it was found that changes in bath temperature of the order of ± .02 C. caused appreciable changes in the potential across the conductivity bridge. This is illustrated by the oscillation of the experimental points in Experiment No. 18, shown on Fig. 8, in which the thermostat was hunting. For any experiments on gas mixtures for which the total change of bridge potential may be of the order of 1 millivolt, it would be essential that the comparison cell and also the current control cell be built into the wall of the cold chamber.

The gas analysis apparatus and method were not good enough to give the desired degree of accuracy of a few hundredths of a percent. The buret was of too large a diameter for the small samples used. If the absorption method is to be retained, an apparatus designed around a

10 cc buret should be used.

For mixtures involving H_2 or CH_4 the gas density method could be used to advantage, assuming the gases used in making up a mixture were thoroughly purified before use. The gases to be analyzed could be transferred from the reaction chambers to the density measuring chamber by means of a mercury-filled aspirator and the necessary pressure adjustment for the density balance obtained by displacement with mercury.

APPENDIX

DERIVATION OF AN EQUATION FOR THE RATE OF THERMAL DIFFUSION IN AN INFINITE LAYER OF A BINARY GAS MIXTURE SUBJECTED TO A TEMPERATURE GRADIENT THROUGH THE LAYER.

The partial differential equation set up previously, Equation (8), is as follows:

$$\frac{\partial (NF_1)}{\partial t} = \frac{\partial}{\partial z}\left\{ ND_c\left[\frac{\partial F_1}{\partial z} + k_T \frac{1}{T}\frac{\partial T}{\partial z}\right]\right\} \qquad (1A)$$

Transformation of this equation is accomplished by use of Equations (11) and (12a), which are given below.

$$\frac{\partial F}{\partial z} = \frac{\partial F}{\partial T}\frac{\partial T}{\partial z} = \frac{Q}{\lambda}\frac{\partial F}{\partial T} \qquad (2A)$$

$$D_c = D_{oc}\left(\frac{T}{T_o}\right)^{1+s}\frac{\rho_o}{\rho}$$

$$\lambda = \lambda_o\left(\frac{T}{T_o}\right)^{s}$$

$$N = \frac{N_o T_o}{T}\frac{\rho}{\rho_o}$$

$$\frac{ND_c}{\lambda} = \frac{N_o D_{oc}}{\lambda_o}$$

As discussed previously, k_T is taken as constant with regard to pressure, temperature, and small changes in composition. Also the temperature gradient is assumed not to change with time so that the molecular density N at any point in the layer is constant with time.

Using Equations (2A) and (3A), Equation (1A) is transformed as follows:

$$N \frac{\partial F_1}{\partial t} = \frac{Q}{\lambda} \frac{\partial}{\partial T} \left(\frac{Q N D_c}{\lambda} \left[\frac{\partial F_1}{\partial T} + \frac{k_T}{T} \right] \right) \qquad (4A)$$

Carrying out the indicated differentiation

$$\frac{\partial F_1}{\partial t} = \left(\frac{Q}{\lambda} \right)^2 D_c \left[\frac{\partial^2 F_1}{\partial T^2} - \frac{k_T}{T^2} \right] \qquad (5A)$$

Using Equation (3A)

$$\left(\frac{Q}{\lambda} \right)^2 D_c = \frac{Q^2 D_{0c}}{\lambda_0^2} \left(\frac{T}{T_0} \right)^{1-s} \frac{\rho_0}{\rho} = E T^{1-s}$$

From kinetic theory the value of s for elastic spheres is 1/2 and for Maxwellian molecules with a repulsive force index of 5 the value of s is 1. Actual gases lie in between these limits (7) (8).

For s = 1, Equation (5A) becomes

$$\frac{\partial F_1}{\partial t} = E \left[\frac{\partial^2 F_1}{\partial T^2} - \frac{k_T}{T^2} \right] \qquad (6A)$$

For s = 1/2, Equation (5A) becomes

$$\frac{\partial F_1}{\partial t} = E T^{\frac{1}{2}} \left[\frac{\partial^2 F_1}{\partial T^2} - \frac{k_T}{T^2} \right] \qquad (7A)$$

The solution of Equation (6A) follows:

At time $t = \infty$ the steady state is reached, at which time $\frac{\partial F_1}{\partial t} = 0$

Then from Equation (6A)

$$\frac{\partial^2 F_1}{\partial T^2} = \frac{k_T}{T^2}$$

Integrating

$$F_1^{\infty} = -k_T \ln T + c_1 T + c_2 \qquad (8A)$$

The flux of molecules of kind 1 as given previously by Equation (2) is

$$N F_1 \underline{v}_1 = -N D_c \left[\frac{\partial F_1}{\partial z} + \frac{k_T}{T} \frac{\partial T}{\partial z} \right] \qquad (9A)$$

In the steady state this flux is zero, so that

$$\frac{\partial F_1}{\partial z} = -\frac{k_T}{T} \frac{\partial T}{\partial z} \qquad (10A)$$

Integrating

$$F_1^{\infty} = -k_T \ln T + c_2 \qquad (11A)$$

The constant c_1 in Equation (9A) is then zero.

The integration of Equation (6A) is to be for the case of an infinite horizontal layer of gas, a binary mixture of thickness h, initially of constant composition with the upper surface of the layer held at the constant temperature T_H and the lower surface at T_c. It is assumed that the temperature gradient exists in the layer at the initial instant.

The boundary conditions are then

1. At time $t = 0$

$$\frac{\partial F_1}{\partial z} = 0$$

2. At $t = \infty$

$$F_1^{\infty} = -k_T \ln T + c_2$$

3. The total number of molecules of each kind is constant. The molecular density at any point in the layer is constant since the temperature gradient is assumed to be constant.

4. The flux of molecules at each end of the tube is zero due to the closed ends. From Equation (10A)

$$\frac{\partial F_1}{\partial z} = \frac{-k_T}{T}\frac{\partial T}{\partial z} \quad \text{at } z = 0,\ z = h.$$

To determine the constant of integration in Equation (11A) the condition is used that the total number of molecules in the layer of gas is constant.

Let F_1^0 = mol fraction of component 1 at $t = 0$.

N = total molecules per unit volume at height z.

N_c = " " " " " " $z = 0$.

The total number of molecules of kind 1 at $t = 0$ per unit of horizontal area is

$$\int_0^h F_1^0 N \, dz$$

At any height z

$$N = N_c \frac{T_c}{T}$$

Also from Equation (10) and Equation (3A)

$$dz = \frac{\lambda}{Q} dT = \frac{\lambda_0}{Q T_0} T dT$$

Then

$$\int_0^h F_1^0 N dz = \frac{F_1^0 N_c T_c \lambda_0}{Q T_0} \int_{T_c}^{T_H} dT$$

$$= \frac{F_1^0 N_c T_c \lambda_0}{Q T_0} \left(T_H - T_c\right) \qquad (12A)$$

At t = ∞ the total number of molecules of kind 1, using Equation (11A), is

$$\int_0^h F_1^\infty N dz = \int_0^h \left(-k_T \ln T + c_2\right) N dz$$

Making substitutions as above, integrating and substituting limits

$$\int_0^h F_1^\infty N dz = \frac{N_c T_c \lambda_0}{Q T_0} \left[-k_T\left(T_H \ln T_H - T_c \ln T_c\right) + k\left(T_H - T_c\right) + c_2\left(T_H - T_c\right)\right] \quad (13A)$$

Equating (12A) and (13A)

$$F_1^{\circ} + k_T\left(\frac{T_H}{T_H - T_c}\ln T_H - \frac{T_c}{T_H - T_c}\ln T_c\right) - k_T = c_2 \qquad (14A)$$

Using this value for c_2, Equation (11A) becomes

$$F_1^{\infty} = -k_T \ln T + F_1^{\circ} + k_T\left(\frac{T_H}{T_H - T_c}\ln T_H - \frac{T_c}{T_H - T_c}\ln T_c - 1\right) \qquad (15A)$$

The integration of Equation (6A) is accomplished by the standard procedure as follows:

$$\frac{\partial F_1}{\partial t} = E\left[\frac{\partial^2 F}{\partial T^2} - \frac{k_T}{T^2}\right]$$

Let $F_1 = u(T,t) + \phi(T)$

Then

$$\frac{\partial u}{\partial t} = E\left[\frac{\partial^2 u}{\partial T^2} + \frac{\partial^2 \phi}{\partial T^2} - \frac{k_T}{T^2}\right]$$

Let $$\frac{\partial^2 \phi}{\partial T^2} = -\frac{k_T}{T^2}$$

Then by integration

$$\phi(T) = -k_T \ln T + c_1 T + c_2$$

and $$\frac{\partial u}{\partial t} = E\,\frac{\partial^2 u}{\partial T^2}$$

Let $u = \psi(t) \cdot \Theta(T)$, then

$$\frac{1}{\psi}\frac{d\psi}{dt} = \frac{E}{\Theta}\frac{d^2\Theta}{dT^2} = -\frac{E\, m^2 \pi^2}{(T_H - T_c)^2}$$

Integrating

$$\Theta = A_m \sin \frac{m\pi(T-T_c)}{T_H - T_c} + B_m \cos \frac{m\pi(T-T_c)}{T_H - T_c}$$

$$\psi = e^{\frac{-E m^2 \pi^2}{(T_H - T_c)^2} t}$$

Assembling terms as required by (16A) and using $c_1 = 0$ and c_2 from Equation (14A)

$$F_1 = \sum e^{\frac{-E m^2 \pi^2}{(T_H - T_c)^2} t} \left[A_m \sin \frac{m\pi(T-T_c)}{T_H - T_c} + B_m \cos \frac{m\pi(T-T_c)}{T_H - T_c} \right]$$

$$- k_T \ln T + k_T \left(\frac{T_H}{T_H - T_c} \ln T_H - \frac{T_c}{T_H - T_c} \ln T_c - 1 \right) + F_1^0 \qquad (17A)$$

Differentiating Equation (17A)

$$\frac{\partial F_1}{\partial z} \doteq \sum_0^\infty + e^{\frac{-E m^2 \pi^2}{(T_H - T_c)^2} t} \frac{m\pi}{T_H - T_c} \left[A_m \cos \frac{m\pi(T-T_c)}{T_H - T_c} - B_m \sin \frac{m\pi(T-T_c)}{T_H - T_c} \right] \frac{\partial T}{\partial z}$$

$$- k_T \frac{1}{T} \frac{\partial T}{\partial z}$$

To meet the fourth boundary condition given previously: $A_m = 0$

$$F_1 = \sum_0^\infty e^{-\frac{E m^2 \pi^2}{(T_H - T_c)^2} t} B_m \cos \frac{m\pi (T - T_c)}{T_H - T_c}$$

$$\cdot -k_T \ln T + k_T \left(\frac{T_H}{T_H - T_c} \ln T_H - \frac{T_c}{T_H - T_c} \ln T_c - 1 \right) + F_1^0 \quad (18A)$$

at $t = 0$, $F_1 = F_1^0$ then

$$B_m \cos \frac{m\pi (T - T_c)}{T_H - T_c} = k_T \ln T - k_T \left(\frac{T_H}{T_H - T_c} \ln T_H - \frac{T_c}{T_H - T_c} \ln T_c - 1 \right)$$

The values of B_m are determined by Fourier expansion in a cosine series. The general expressions for the coefficients are

$$\frac{B_0}{2} = \frac{1}{c} \int_0^c f(x)\, dx$$

$$B_m = \frac{2}{c} \int_0^c f(x) \cos \frac{m\pi x}{c}\, dx \qquad (19A)$$

Then for the present case

$$\frac{B_0}{2} = \frac{k_T}{T_H - T_c} \int_{T_c}^{T_H} \left(\ln T - \frac{T_H}{T_H - T_c} \ln T + \frac{T_c}{T_H - T_c} \ln T_c + 1 \right) dT \quad (20A)$$

Integrating Equation (20A) and substituting limits

$$\frac{B_0}{2} = 0 \qquad (21A)$$

Values for B_m are determined as follows:

$$B_m = \frac{2}{T_H-T_c}\int_{T_c}^{T_H}\left[k_T \ln T - k_T A\right]\cos\frac{m\pi(T-T_c)}{T_H-T_c}\,dT$$

Where $A = \frac{T_H}{T_H-T_c}\ln T_H - \frac{T_c}{T_H-T_c}\ln T_c - 1$

Integrating by parts

$$B_m = 2\Big|_{T_c}^{T_H}\left[k_T \ln T - k_T A\right]\left[\sin\frac{m\pi(T-T_c)}{T_H-T_c}\right]\left[\frac{T_H-T_c}{m\pi(T_H-T_c)}\right]$$

$$-2\int\frac{1}{m\pi}\sin\frac{m\pi(T-T_c)}{(T_H-T_c)}\,.\,k_T\frac{dT}{T} \qquad 22A$$

Substituting limits in the 1st term reduces it to zero.

Expanding the 2nd term of Equation (22A):

$$B_m = -2k_T\int_{T_c}^{T_H}\frac{1}{m\pi}\cos\frac{m\pi T_c}{T_H-T_c}\sin\frac{m\pi T}{T_H-T_c}\frac{d\left(\frac{m\pi T}{T_H-T_c}\right)}{\frac{m\pi T}{T_H-T_c}}$$

$$-2k_T\int_{T_c}^{T_H}\frac{1}{m\pi}\sin\frac{m\pi T_c}{T_H-T_c}\cos\frac{m\pi T}{T_H-T_c}\frac{d\left(\frac{m\pi T}{T_H-T_c}\right)}{\frac{m\pi T}{T_H-T_c}} \qquad (23A)$$

$$\int_0^x \frac{\sin u}{u}\,du = \text{sine integral} = \text{Si}\,(u)$$

$$-\int_x^\infty \frac{\cos u}{u}\,du = \text{cosine integral} = \text{Ci}\,(u)$$

$$B_m = 2k_T\left[\frac{1}{m\pi}\cos\frac{m\pi T_c}{T_H-T_c}\left(\text{Si}\,\frac{m\pi T_H}{T_H-T_c} - \text{Si}\,\frac{m\pi T_c}{T_H-T_c}\right)\right]$$

$$-2k_T\left[\frac{1}{m\pi}\sin\frac{m\pi T_c}{T_H-T_c}\left(\text{ci}\,\frac{m\pi T_H}{T_H-T_c} - \text{ci}\,\frac{m\pi T_c}{T_H-T_c}\right)\right] \quad (24A)$$

The final solution for Equation (6A) is then:

$$F_1 = \sum_1^\infty e^{\frac{-Em^2\pi^2}{(T_H-T_c)^2}t}\, B_m \cos\frac{m\pi(T-T_c)}{T_H-T_c}$$

$$-k_T \ln T + k_T\left(\frac{T_H}{T_H-T_c}\ln T_H - \frac{T_c}{T_H-T_c}\ln T_c - 1\right) + F_1^0 \quad (25A)$$

Where B_m is given by Equation (24A) and E is evaluated by Equation (2A) and (3A) as follows:

$$Qh = \int \lambda\, dT = \int_{T_c}^{T_H} \frac{\lambda_0}{T_0}\, T\, dT = \frac{1}{2}\,\frac{\lambda_0}{T_0}\left(T_H^2 - T_c^2\right)$$

$$E = \frac{Q^2 D_{oc}}{\lambda_0^2}\,\frac{1}{T_0^{1-s}}\,\frac{\rho_0}{\rho} = \frac{T_H^2 - T_c^2}{4h^2 T_0^2}\, D_{oc}\,\frac{\rho_0}{\rho}$$

The exponent then has the value:

$$\frac{E m^2 \pi^2}{(T_H - T_c)^2} = \frac{(T_H^2 - T_c^2)^2}{(T_H - T_c)^2} \cdot \frac{D_{oc}}{4 h^2 T_0^2} \cdot \frac{\rho_0}{\rho} m^2 \pi^2 \quad (26A)$$

The composition-time curve for a 50-50 carbon dioxide-hydrogen layer at one atmosphere pressure, 15.87 cm thick, with the upper surface held at 600° K. and the lower surface at 300° K, is calculated in the following. The values of $k_T = 0.083$ and $D_{oc} = 0.550$ are used.

The value of the exponent is

$$\frac{E m^2 \pi^2}{(T_H - T_c)^2} = 0.0586\ m^2$$

The constant term in Equation (25A) is:

$$k_T \left(\frac{T_H}{T_H - T_c} \ln T_H - \frac{T_c}{T_H - T_c} \ln T_c - 1 \right) + F_1^{\circ} = 1.0055$$

For $T_H = 600°$ K. and $T_c = 300°$ K., the second term of B_m, as given by Equation (24A), becomes zero, then

$$B_m = -2 k_T \left[\frac{1}{m\pi} \cos m\pi \left(\mathrm{Si}\, 2m\pi - \mathrm{Si}\, m\pi \right) \right]$$

Using values of the sine integral, tabulated by Glaisher (9), the numerical values of the coefficients for the first eight terms are as follows:

$B_1 = -.022920$

$B_2 = -.001955$

$B_3 = -.002760$

$B_4 = -.000515$

$B_5 = -.001003$

$B_6 = -.000231$

$B_7 = -.000513$

$B_8 = -.000130$

With numerical coefficients inserted, Equation (25A) becomes:

$$\begin{aligned} F_1 = \sum & -0.02292 \cos \frac{\pi(T-300)}{300} \cdot e^{-0.0586t} \\ & -0.00195 \cos \frac{2\pi(T-300)}{300} \cdot e^{-0.2344t} \\ & -0.00276 \cos \frac{3\pi(T-300)}{300} \cdot e^{-0.5274t} \\ & -0.00052 \cos \frac{4\pi(T-300)}{300} \cdot e^{-0.9376t} \\ & - - - - - - - - \\ & -0.083 \ln T + 1.0055 \end{aligned} \qquad (26A)$$

The calculated results for various temperatures are shown in Figure 13 as composition versus time curves, and in Figure 14 curves of compositions, throughout the layer at given periods after the start, are shown. It is to be noted from this latter figure that the change from the initial assumed conditions of uniform composition to the final steady state condition is practically complete in sixty seconds. Therefore the assumption made previously that the steady state condition exists at all times in the connecting tube of the two-chamber apparatus seems reasonable.

The variation of the coefficient of thermal conductivity λ given by Equation (3A) and the assumption of s = 1 establish the temperature gradient as given by the following:

$$\frac{z}{h} = \frac{T^2 - T_c^2}{T_H^2 - T_c^2} \qquad (27A)$$

As a point of incidental interest, for the temperature gradient given by Equation (27A) half of the total number of molecules in the layer are above and half below the mid-temperature plane, in this case 450° K. This plane is situated 41.6% of the distance from the lower to the upper surfaces of the layer. Figure 14 shows that the mid-temperature plane is not a point of symmetry and in fact, according to this solution of the problem, no stationary point of symmetry exists for the thermal diffusion process.

The assumption of s = 1/2 for hard spheres gives Equation (7A).

The solution of this equation by the general method given by Karman and Biot (10) is as follows:

$$F_1 = \sum_0^\infty e^{-En^2t}\left[A_n\left(\frac{4}{3}nT^{3/4}\right)^{\frac{2}{3}}J_{\frac{2}{3}}\left(\frac{4}{3}nT^{3/4}\right) + B_n\left(\frac{4}{3}nT^{3/4}\right)^{\frac{2}{3}}J_{-\frac{2}{3}}\left(\frac{4}{3}nT^{3/4}\right)\right.$$

$$\left. - k_T \ln T + k_T\left[\frac{T_H^{\frac{1}{2}}}{T_H^{\frac{1}{2}}-T_C^{\frac{1}{2}}}\ln T_H - \frac{T_C^{\frac{1}{2}}}{T_H^{\frac{1}{2}}-T_C^{\frac{1}{2}}}\ln T_C - 2\right]\right. + F_1^{\,0}$$

The evaluation of the constants A_n and B_n to fit the boundary conditions was not accomplished.

REFERENCES

(1) Chapman and Cowling -- Mathematical Theory of Non Uniform Gases -- Cambridge Press, (1939) Page 244.

(2) Furry, Jones and Onsager -- On the Theory of Isotope Separation by Thermal Diffusion Physical Review 55, 1083, (1939)

(3) Ibbs, Grew and Hirst -- Proc. Phys. Soc. 41, 456 (1929)

(4) Schmahl and Schewe -- Zeit f. Elektrochemie 46, 203 (1940)

(5) Lugg -- Phil. Mag. 8, 1019 (1929)

(6) Palmer and Weaver -- Thermal Conductivity Method for the Analysis of Gases -- Technologic Papers of the Bureau of Standards No. 249

(7) Reference (1) Page 249.

(8) Jeans -- The Kinetic Theory of Gases -- Cambridge Press, (1940) Page 174.

(9) Glaisher -- Phil. Trans. Roy. Soc. 160, 367 (1870)

(10) Karman and Biot -- Mathematical Methods in Engineering -- McGraw Hill (1940)

A complete list of references up to 1940 on thermal diffusion is given by reference (4) above.

PROPOSITIONS

1. The rate of thermal diffusion in a two-chamber apparatus is affected by the nature of the temperature gradient in the connecting tube.

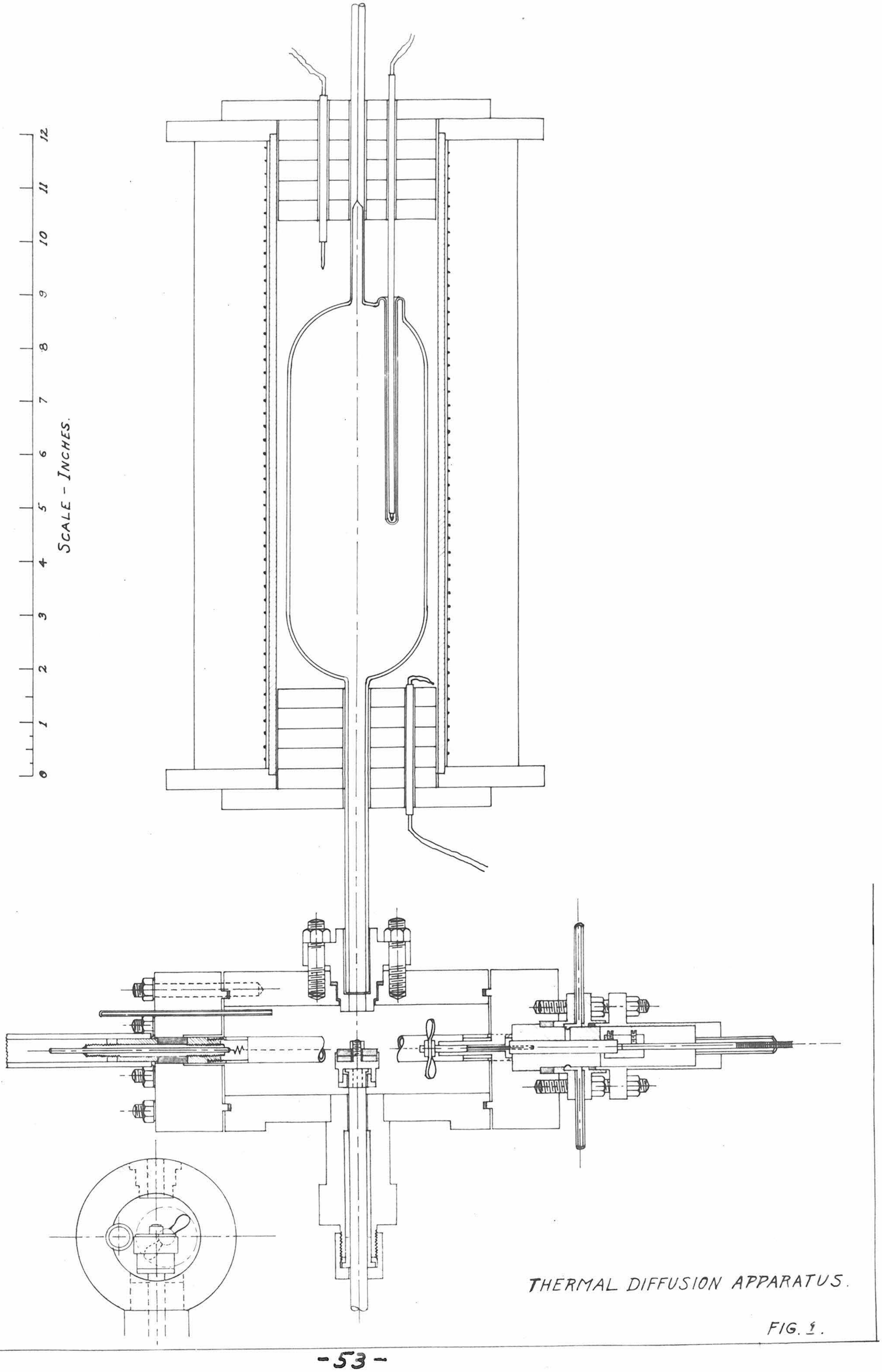
2. In a hydrocarbon gas mixture, such as a natural gas, the ethane and heavier constituents may be removed by scrubbing with butane at a temperature above the dew point of the natural gas for given pressure conditions.

3. The development of an econimical process for the synthesis of ethane from methane is an important research problem.

4. A bubble-point pressure versus temperature curve for a multicomponent hydrocarbon mixture can be determined by measurement of the Joule Thomson effect.

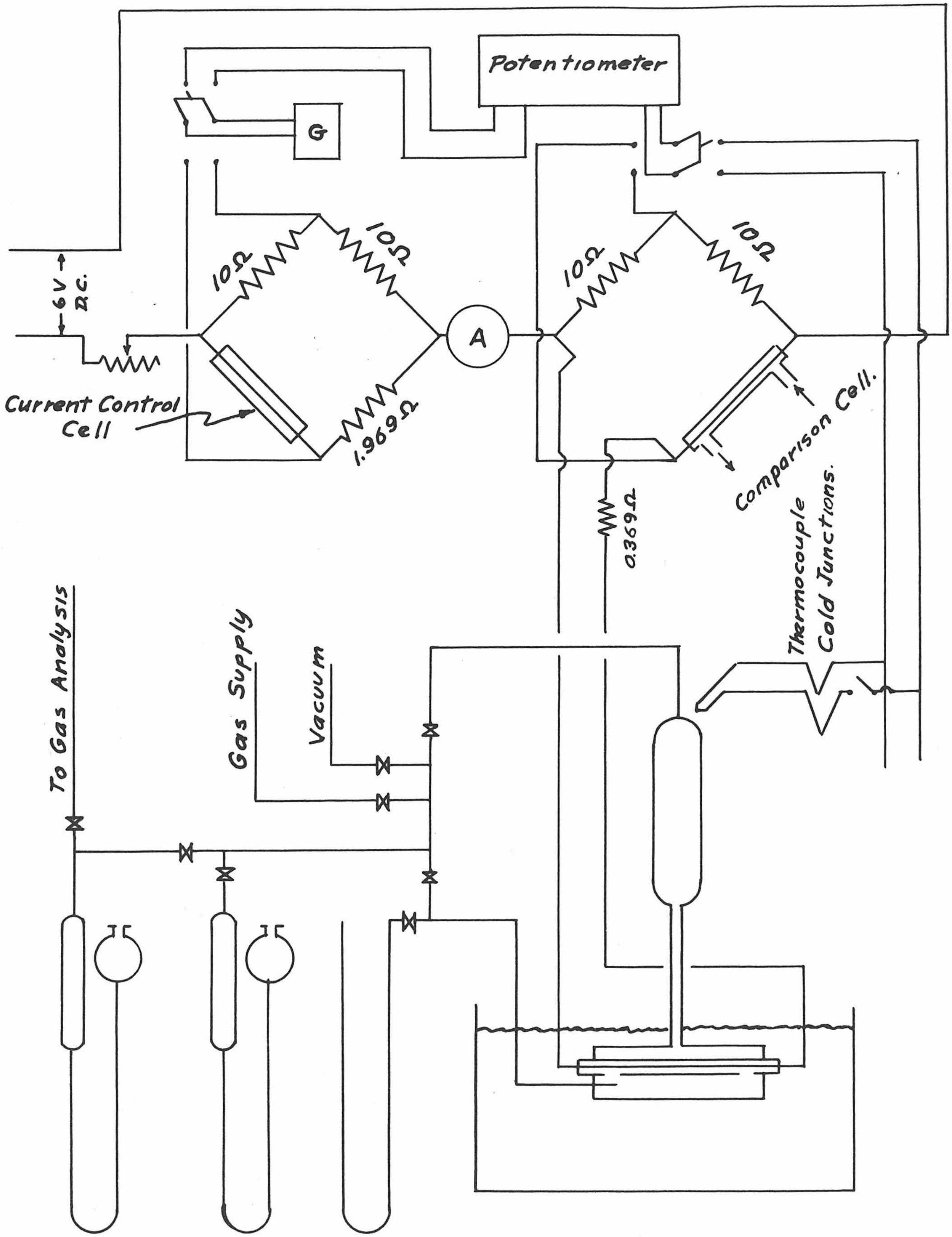
5. A high compression temperature may be developed in a Diesel engine without a concurrent high compression pressure.

6. Jacobs and Collins (Jl. Applied Physics, Vol. 11, No. 7, pp 491-95, July, 1940) discuss the efficiency of heat exchangers for hydrogen liquefaction in terms of terminal temperature differences. Such a criterion has little significance if liquefaction is occurring in the high pressure channel of the heat exchanger.



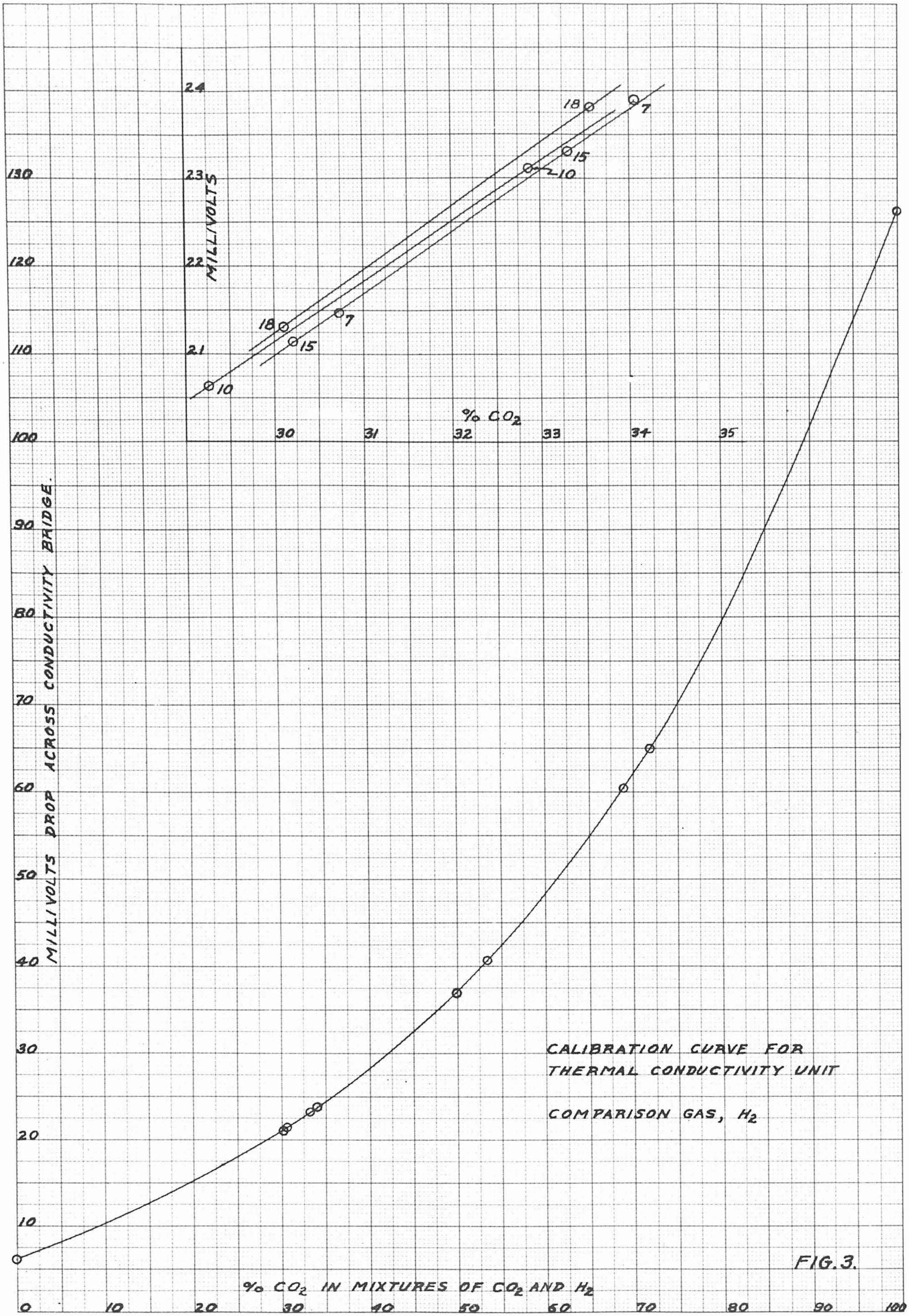
THERMAL DIFFUSION APPARATUS.

FIG. 1.



WIRING and FLOW DIAGRAM.

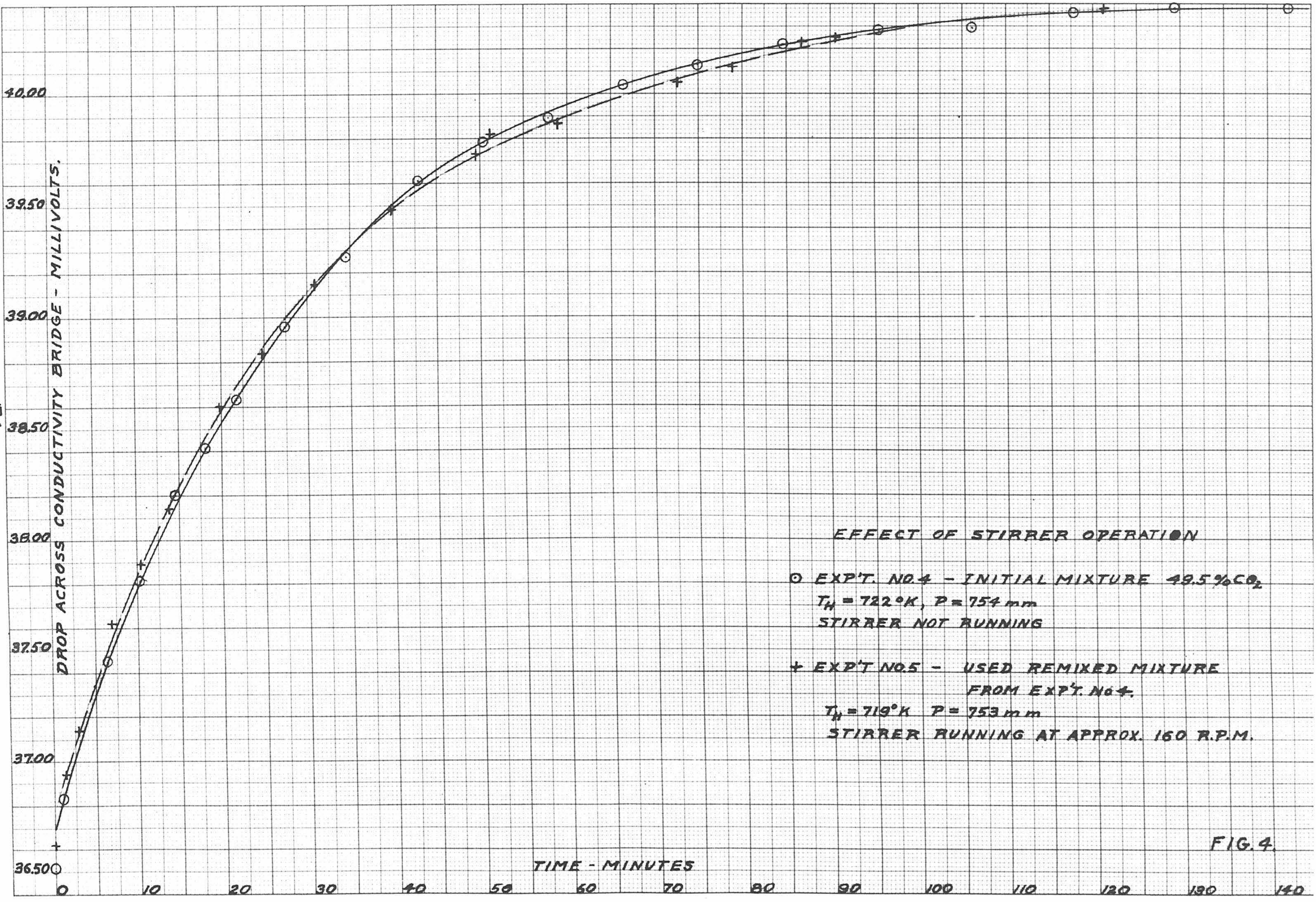
FIG. 2.



CALIBRATION CURVE FOR
THERMAL CONDUCTIVITY UNIT

COMPARISON GAS, H_2

FIG. 3.

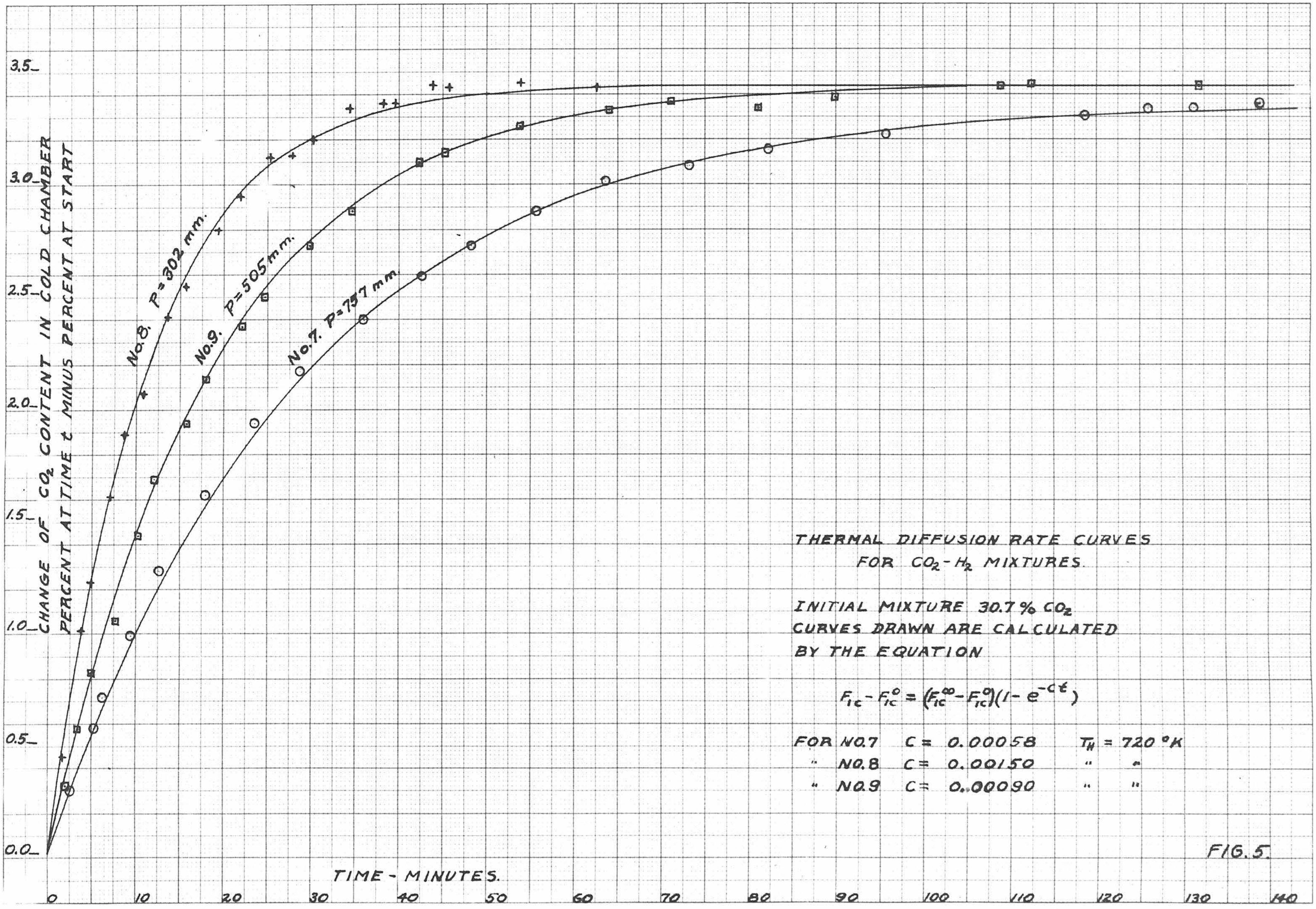


EFFECT OF STIRRER OPERATION

⊙ EXP'T. NO.4 - INITIAL MIXTURE 49.5 % CO_2
T_H = 722 °K, P = 754 mm
STIRRER NOT RUNNING

+ EXP'T NO.5 - USED REMIXED MIXTURE
FROM EXP'T. No 4.
T_H = 719° K P = 753 mm
STIRRER RUNNING AT APPROX. 160 R.P.M.

FIG. 4.



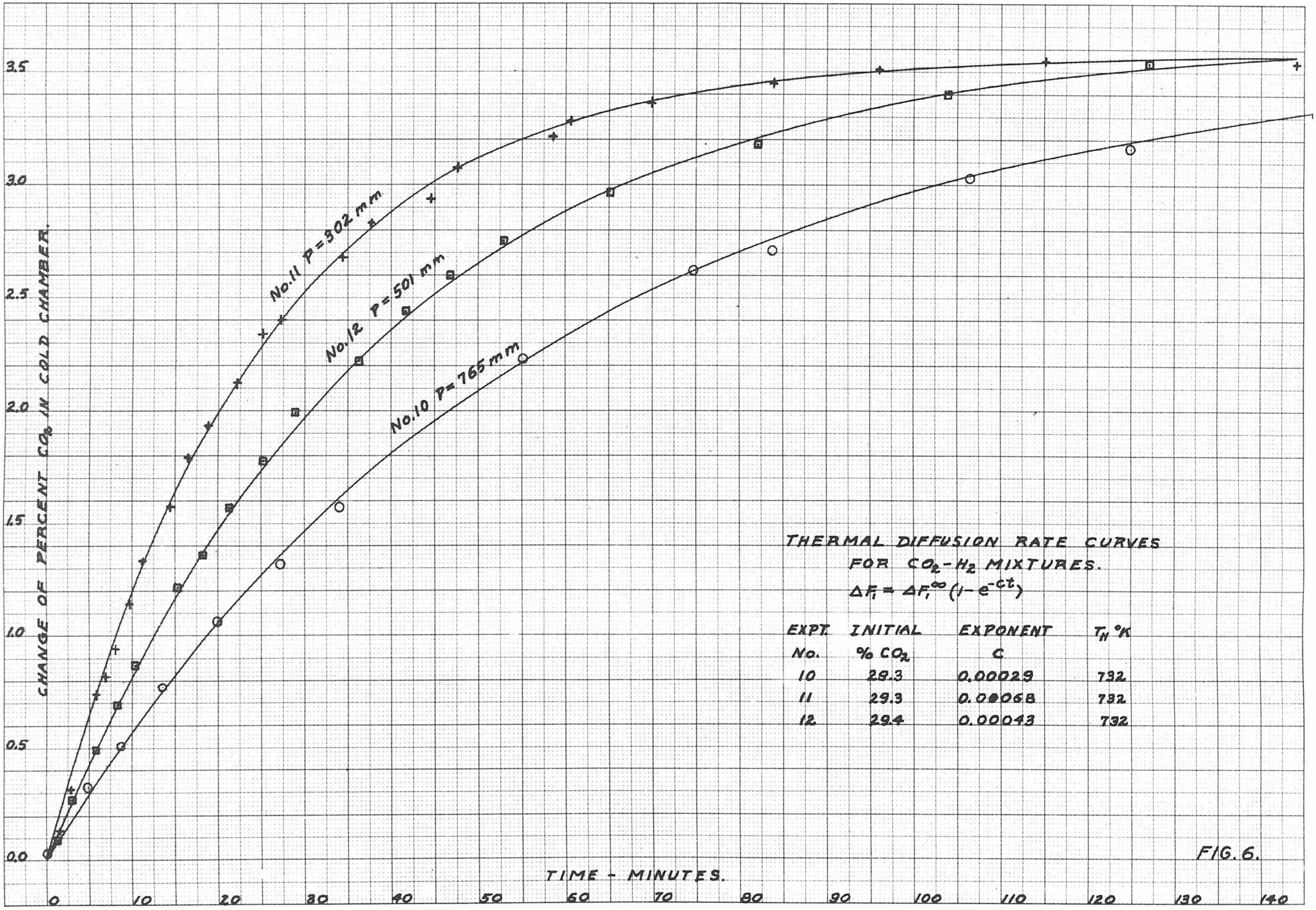
THERMAL DIFFUSION RATE CURVES
FOR CO_2-H_2 MIXTURES.

INITIAL MIXTURE 30.7 % CO_2
CURVES DRAWN ARE CALCULATED
BY THE EQUATION

$$F_{1c} - F_{1c}^{0} = (F_{1c}^{\infty} - F_{1c}^{0})(1 - e^{-ct})$$

FOR NO.7	C = 0.00058	T_H = 720 °K
" NO.8	C = 0.00150	" "
" NO.9	C = 0.00090	" "

FIG. 5.

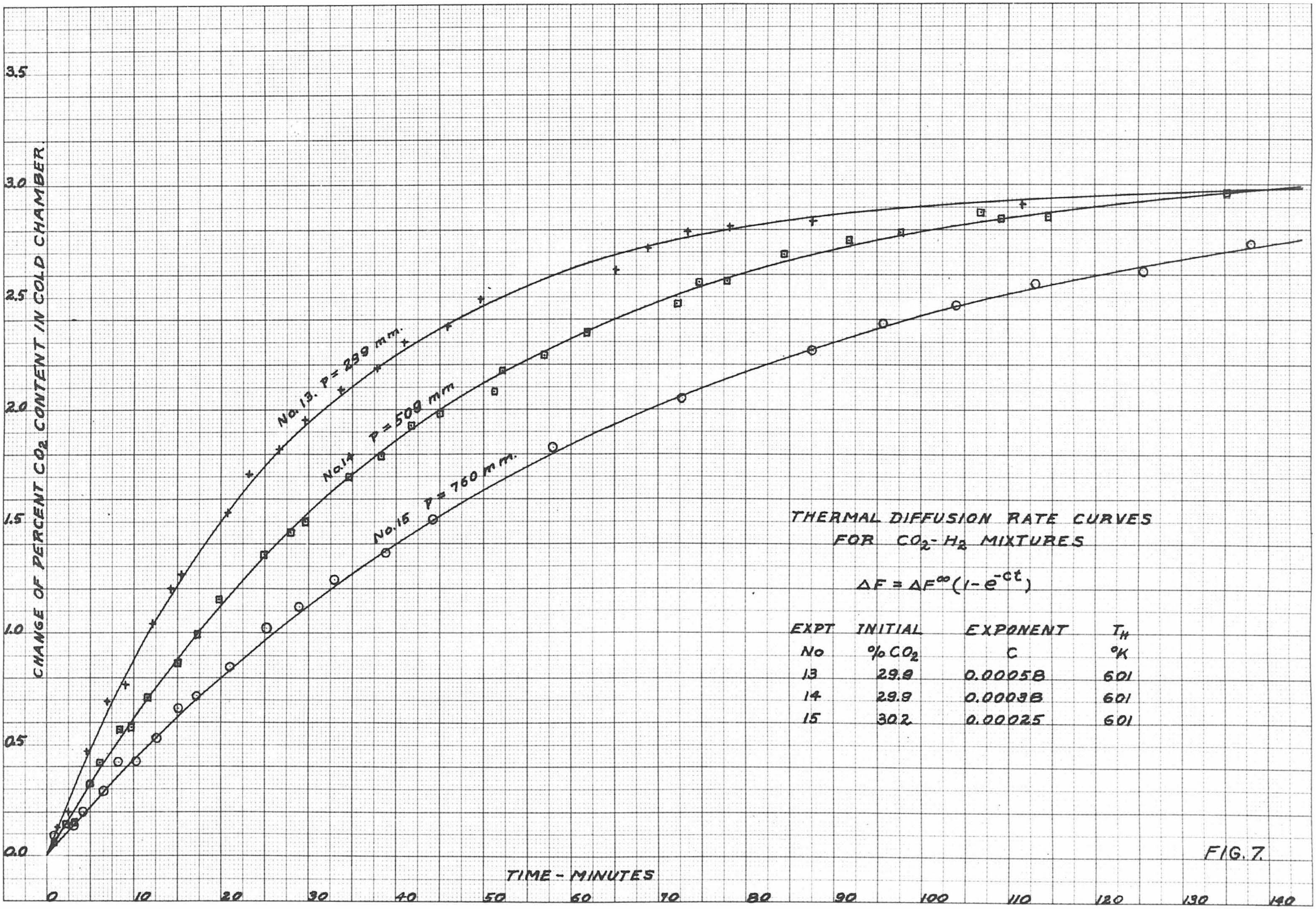


THERMAL DIFFUSION RATE CURVES
FOR CO_2-H_2 MIXTURES.

$\Delta F_1 = \Delta F_1^{\infty}(1-e^{-ct})$

EXPT. No.	INITIAL % CO_2	EXPONENT C	T_H °K
10	29.3	0.00029	732
11	29.3	0.00068	732
12	29.4	0.00043	732

FIG. 6.

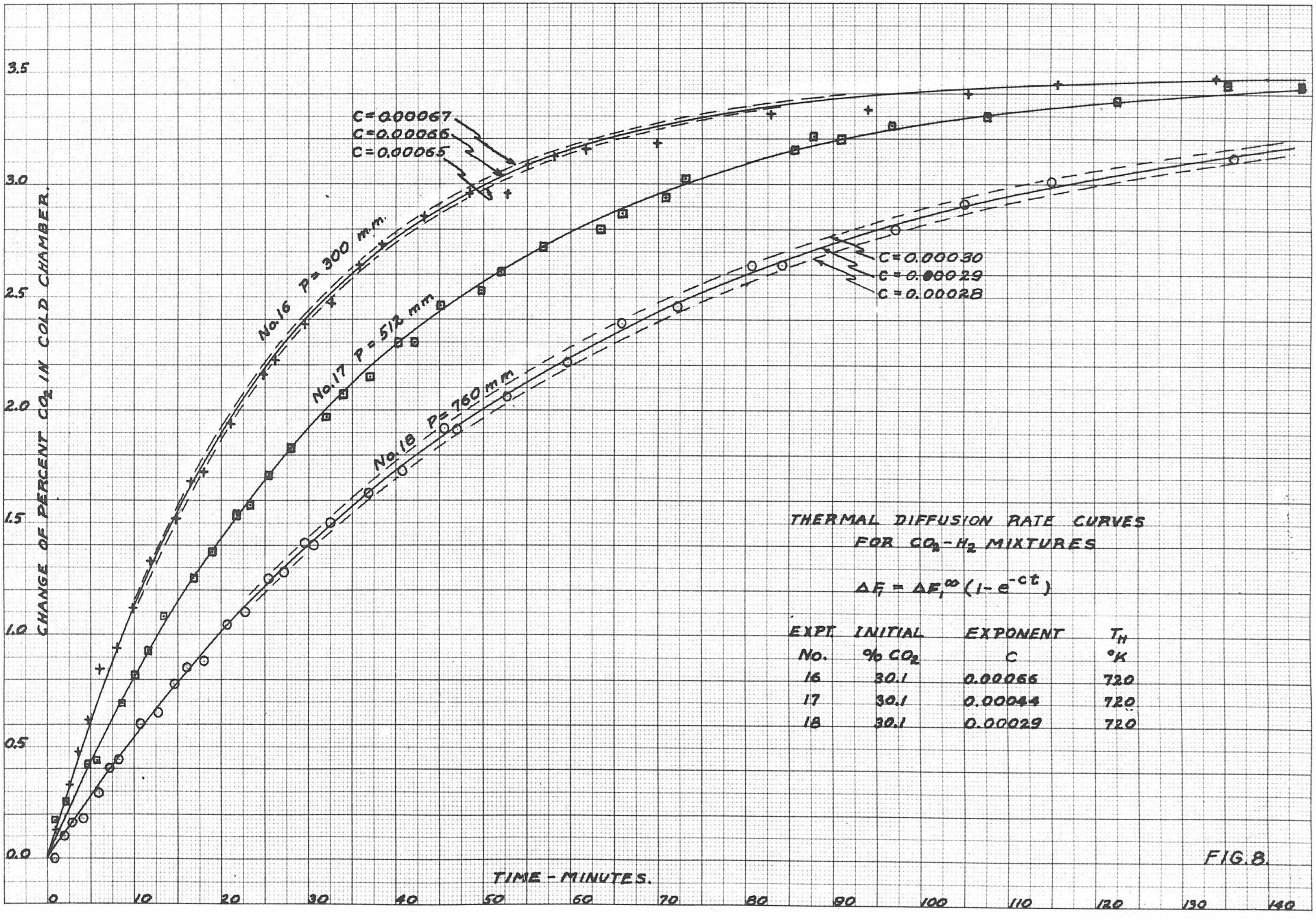


THERMAL DIFFUSION RATE CURVES
FOR CO_2- H_2 MIXTURES

$$\Delta F = \Delta F^{\infty}(1 - e^{-ct})$$

EXPT No	INITIAL % CO_2	EXPONENT C	T_H °K
13	29.9	0.00058	601
14	29.9	0.00038	601
15	30.2	0.00025	601

FIG. 7.

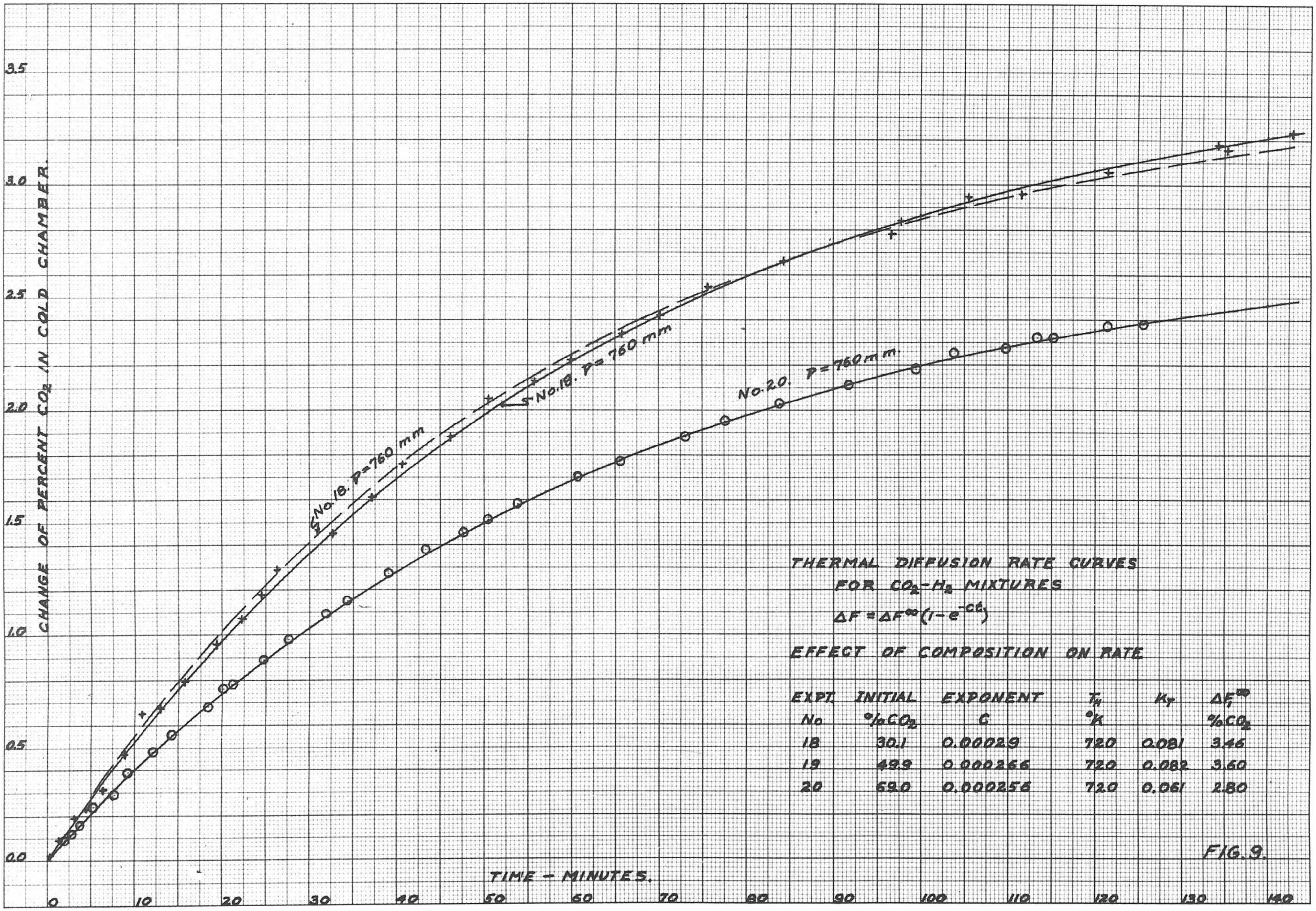


THERMAL DIFFUSION RATE CURVES
FOR CO_2-H_2 MIXTURES

$$\Delta F_1 = \Delta F_1^{\infty}(1 - e^{-ct})$$

EXPT. No.	INITIAL % CO_2	EXPONENT C	T_H °K
16	30.1	0.00066	720
17	30.1	0.00044	720
18	30.1	0.00029	720

FIG. 8.



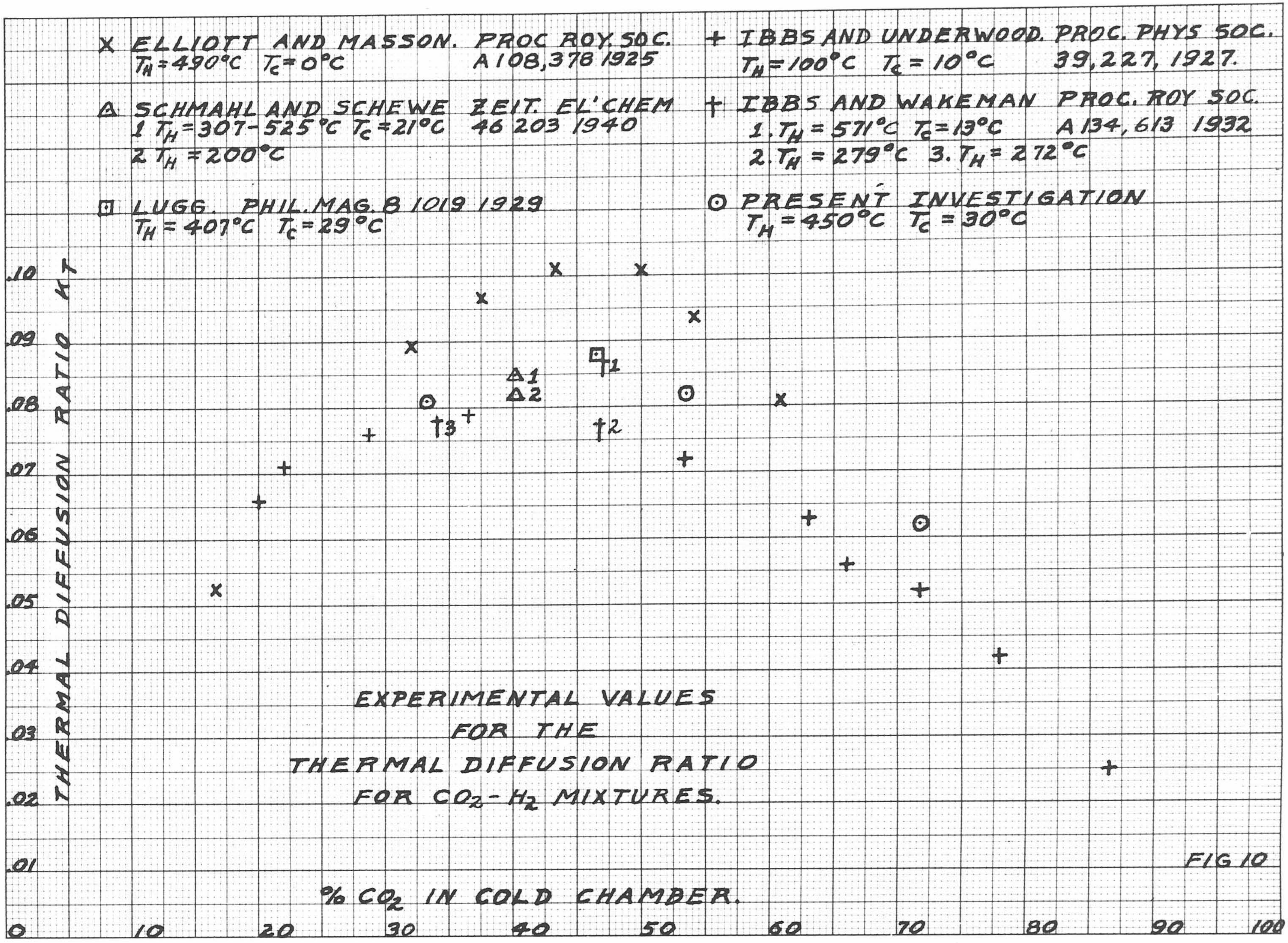
THERMAL DIFFUSION RATE CURVES
FOR CO_2-H_2 MIXTURES

$\Delta F = \Delta F^{\infty}(1 - e^{-ct})$

EFFECT OF COMPOSITION ON RATE

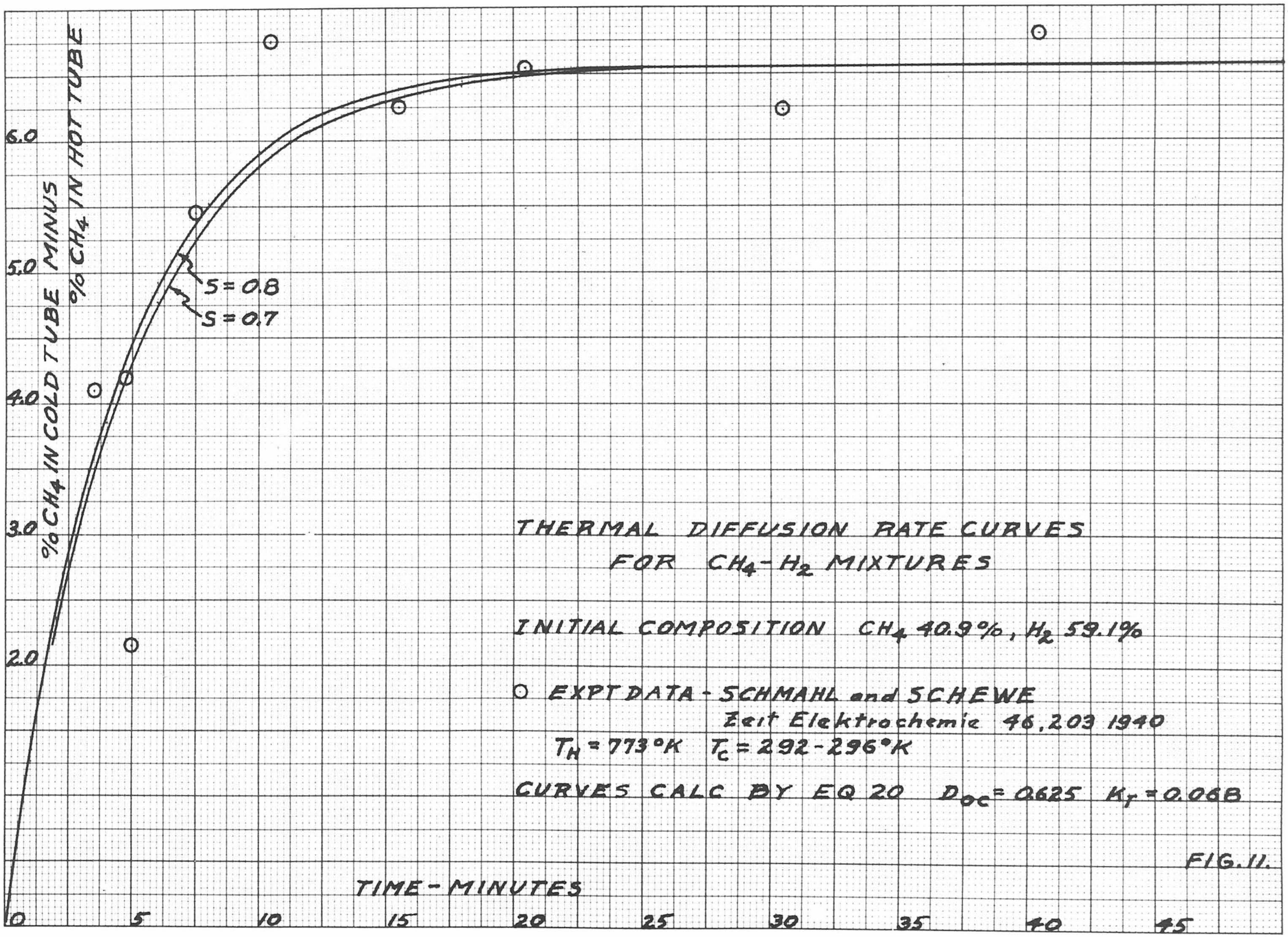
EXPT. No	INITIAL %CO_2	EXPONENT C	T_H °K	K_T	ΔF_1^{∞} %CO_2
18	30.1	0.00029	720	0.081	3.46
19	49.9	0.000266	720	0.082	3.60
20	69.0	0.000256	720	0.061	2.80

FIG. 9.



EXPERIMENTAL VALUES
FOR THE
THERMAL DIFFUSION RATIO
FOR CO_2-H_2 MIXTURES.

FIG 10



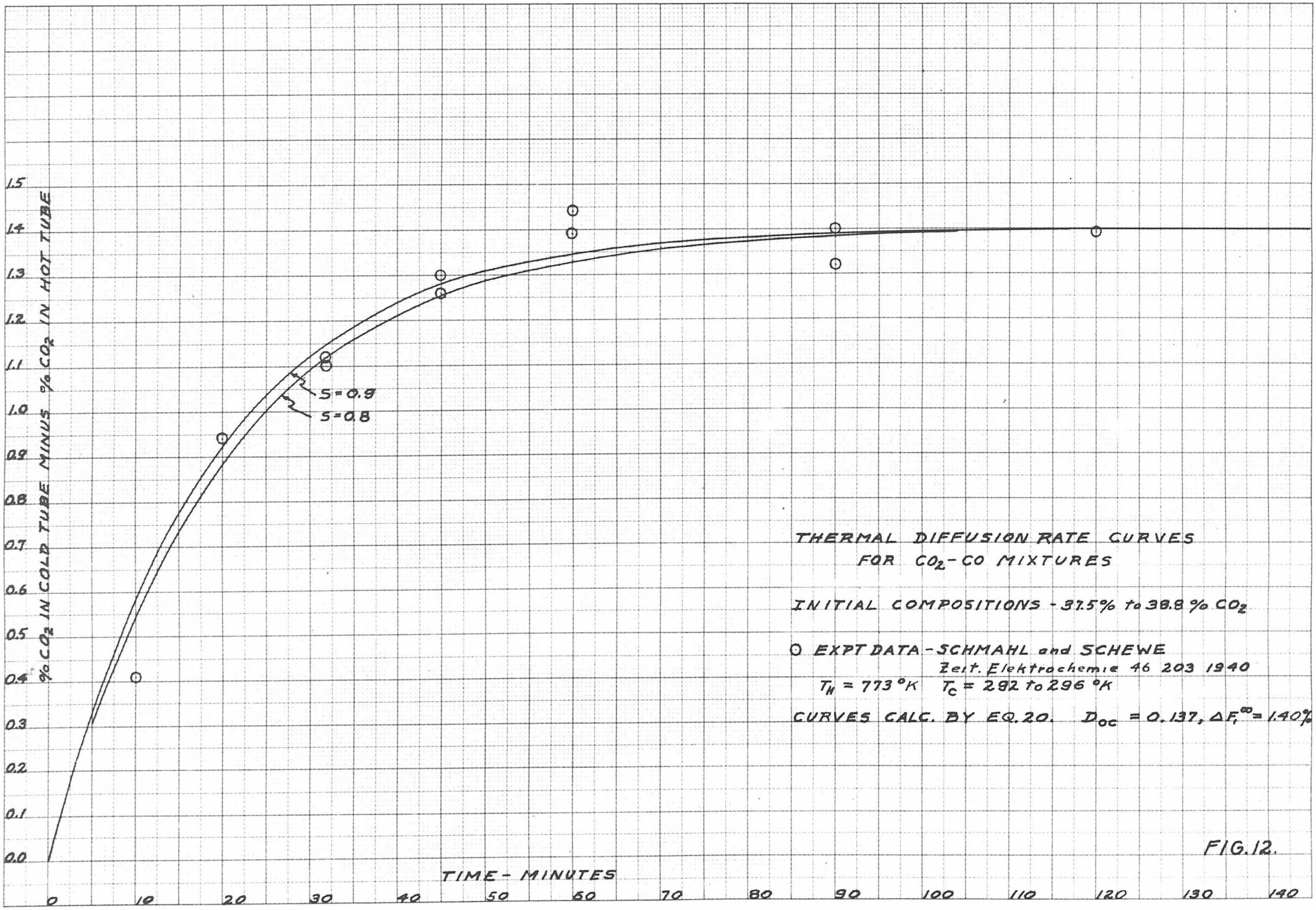
THERMAL DIFFUSION RATE CURVES
FOR CH_4-H_2 MIXTURES

INITIAL COMPOSITION CH_4 40.9%, H_2 59.1%

○ EXPT DATA - SCHMAHL and SCHEWE
Zeit Elektrochemie 46, 203 1940
T_H = 773°K T_C = 292-296°K

CURVES CALC BY EQ 20 D_{oc} = .0625 K_T = 0.068

FIG. 11.



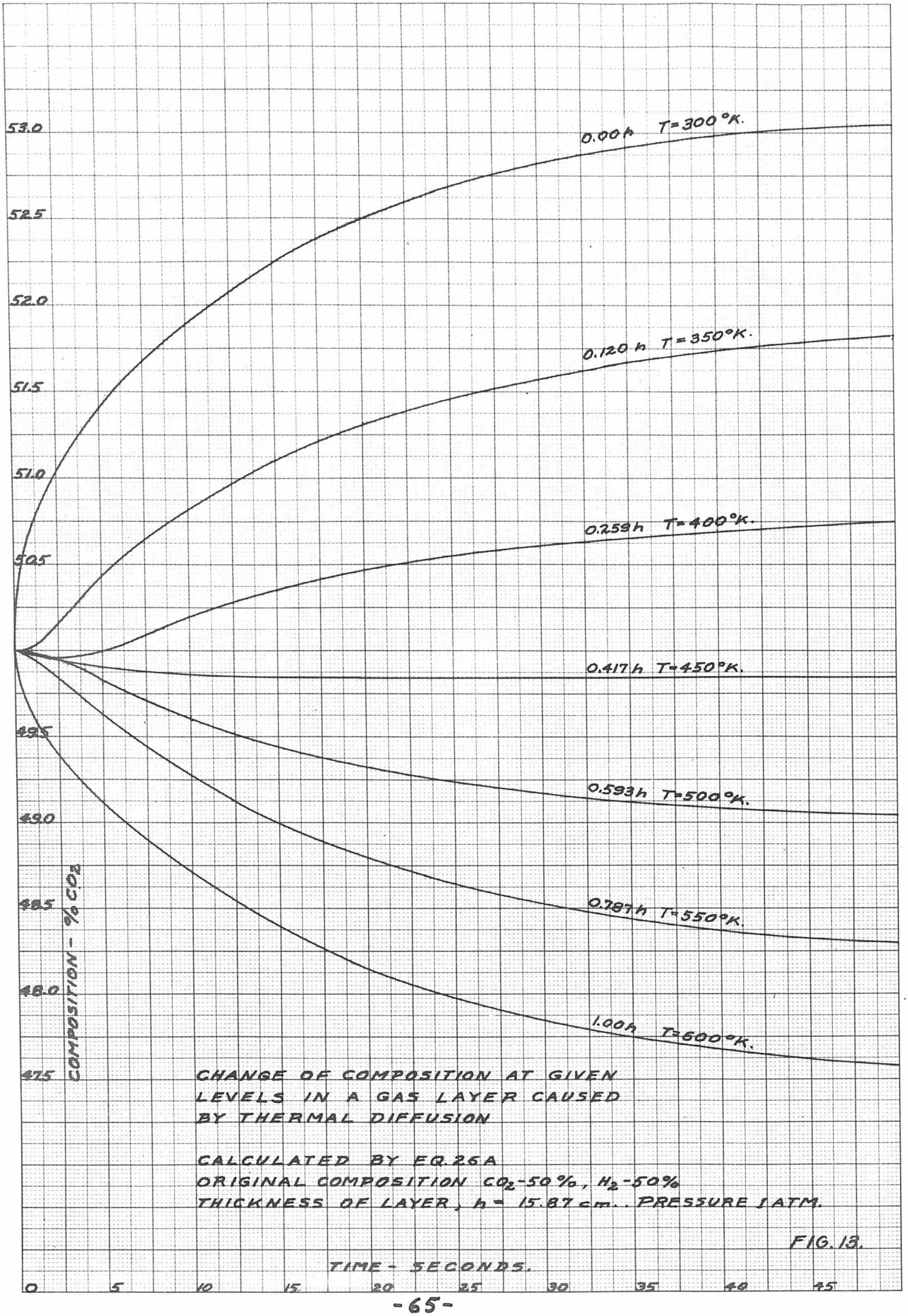
THERMAL DIFFUSION RATE CURVES
FOR CO_2 - CO MIXTURES

INITIAL COMPOSITIONS - 37.5% to 38.8% CO_2

○ EXPT DATA - SCHMAHL and SCHEWE
Zeit. Elektrochemie 46 203 1940
T_H = 773 °K T_C = 282 to 296 °K

CURVES CALC. BY EQ. 20. $D_{oc} = 0.137$, $\Delta F_1^{\infty} = 1.40\%$

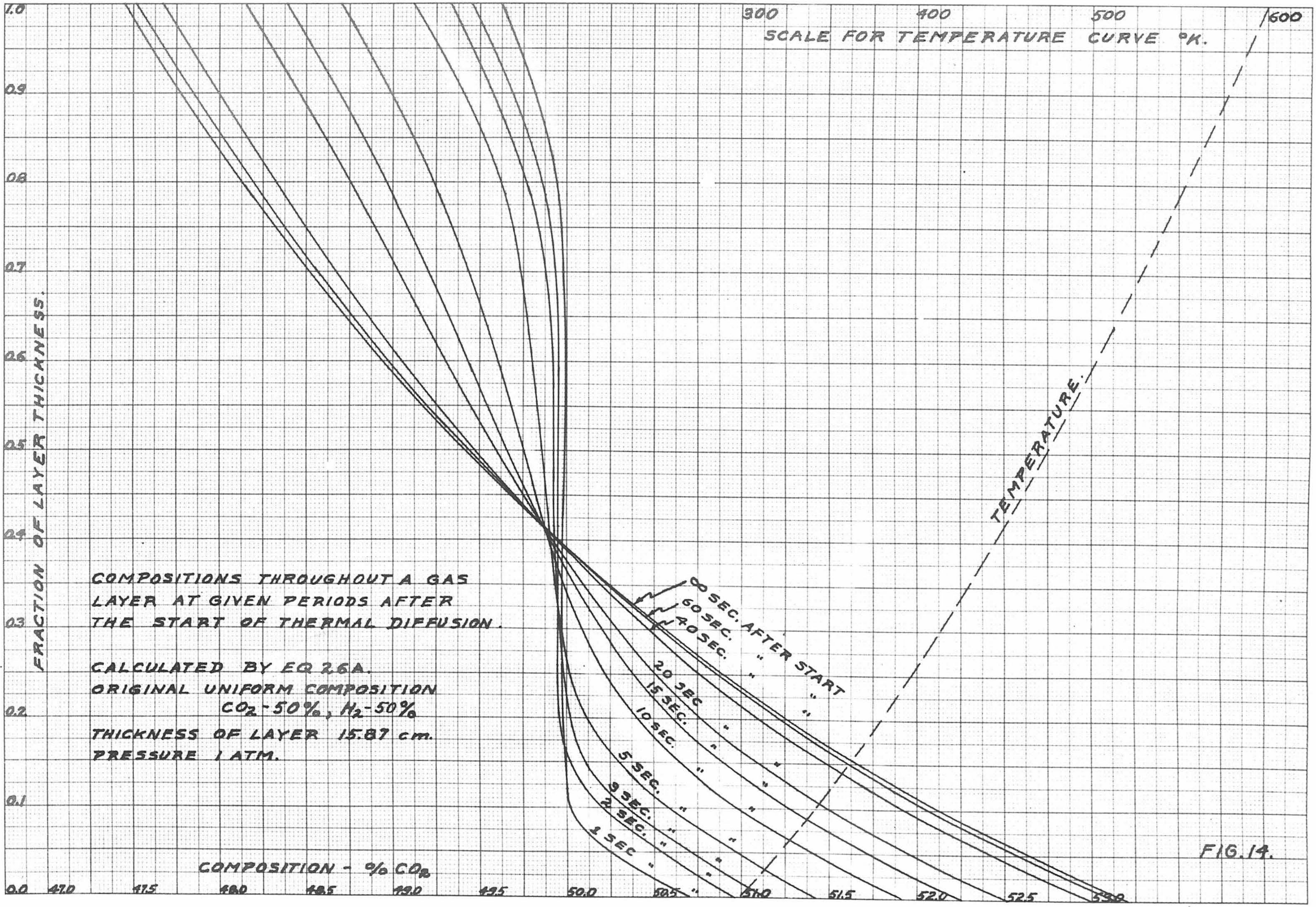
FIG. 12.



CHANGE OF COMPOSITION AT GIVEN LEVELS IN A GAS LAYER CAUSED BY THERMAL DIFFUSION

CALCULATED BY EQ. 26A
ORIGINAL COMPOSITION CO_2 - 50 %, H_2 - 50 %
THICKNESS OF LAYER, h = 15.87 cm. PRESSURE 1 ATM.

FIG. 13.



COMPOSITIONS THROUGHOUT A GAS
LAYER AT GIVEN PERIODS AFTER
THE START OF THERMAL DIFFUSION.

CALCULATED BY EQ 26A.
ORIGINAL UNIFORM COMPOSITION
CO_2 - 50%, H_2 - 50%
THICKNESS OF LAYER 15.87 cm.
PRESSURE 1 ATM.

FIG. 14.