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A Thermal Conductivity Method for the Determination of Isotopic Exchanges in the Simpler Gaseous Molecules

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A simple high pressure thermal conductivity gauge of good mechanical stability, freedom from poisoning effects and high accuracy has been described in detail. Its physical characteristics have been studied and optimum conditions for operation indicated. Its applicability to a wide variety of analyses is discussed and specific data quoted for those

of the isotopic isomers of the lower aliphatic hydrocarbons and the hydrogens. Methods of direct calibration for the latter substances are indicated as well as a technique for their separation and purification. The theory of the gauge is developed and compared with experimental observations on the hydrogen isotopes.

SINCE the discovery of the heavy hydrogen isotope, deuterium, and its use by the physical chemist as an aid in elucidating the kinetics of reactions several workers in the field have developed thermal conductivity gauges for the purpose of isotopic analysis. In general they were operated with mixtures of the hydrogens, advantage being taken of the large specific heat differences which exist between the isotopic molecules H_2 , HD and D_2 at low temperatures—such as those in the liquid-air region. Both high and low gas pressures have been employed. An adequate review of the early work in this field is to be found in A. Farkas' book *Light and Heavy Hydrogen*. Subsequent to the work included above, Sachsse and Bratzler¹ developed a thermal gauge, for use on the hydrogen isotopes, which operated at high pressures (~ 200 mm) and room temperatures, thus making direct use of the differences in thermal conductance due alone to the mass differences involved. They claimed high precision for their gauge. Still more recently Reitz and Bonhoeffer² have published results obtained with a Pirani manometer whereby the analysis is carried out directly upon samples of isotopic water vapor.

Our experiences with several of the above-mentioned types of gauges³ showed quite definitely that they possessed characteristics which made them difficult to operate. Recently Wirtz⁴ published a paper indicating some of these

difficulties attendant upon the Farkas low pressure gauge. The accommodation coefficient plays a dominant role in such low pressure gauges and, as is well known to workers in this field, is a very temperamental factor placing serious limitations on the attainable accuracy. With these difficulties in mind we attempted to develop a simple thermal gauge—operating at higher pressures so as to eliminate accommodation coefficient effects—of rugged construction and yet of sufficiently high reproducibility and precision that it could be used to analyze directly the amounts of isotopic exchanges in the simpler compound gaseous molecules.

It is felt that the results to be presented in this paper adequately show that all these characteristics have been attained. Our gauge has been used with completely satisfactory results in a series of recent researches involving exchange reactions,^{5, 6} and has proved itself a practical tool. Because of the difficulties which seem to be encountered in the construction and operation of this type of analytical device it was deemed advisable to describe our gauge in detail. For these reasons it is felt that its publication may prove of value to other workers in the field.

THE APPARATUS

The gauge itself, Fig. 1, consists of a fine bare platinum wire A (0.0008 inch diam.) mounted coaxially in a $\frac{1}{8}$ -inch hole bored through the center of a $\frac{1}{2}$ -inch rolled brass rod B . The

¹ Sachsse and Bratzler, *Zeits. f. physik. Chemie* **171A**, 332 (1934).

² Reitz and Bonhoeffer, *Zeits. f. physik. Chemie* **174A**, 427 (1935).

³ Mr. E. A. Smith and others, private communication.

⁴ K. Wirtz, *Zeits. f. physik. Chemie* **32B**, 334 (1936).

⁵ Trenner, Morikawa and Taylor, *J. Chem. Phys.* **5**, 203 (1937).

⁶ Morikawa, Trenner and Taylor, *J. Am. Chem. Soc.*, in press.

brass rod is 6 inches long and the platinum wire $4\frac{7}{8}$ inches long. The wire *A* is held concentric by means of the recessed Bakelite bushing *C* through the centers of which it passes, tiny holes being provided for that purpose. These holes are of a size just sufficient to permit the two heavy platinum leads (No. 28 B & S gauge) *D* to pass through them. The lower lead-in *D* passes out through the brass bushing *E* and the whole is soldered into the bottom of the brass rod *B*. The upper bushing *C* is bored with a second hole by means of a No. 50 drill and is located off center. This hole permits free entry and exit of the gases introduced into the gauge. Above the upper lead-in wire is a tungsten spring *F* (\sim diameter 5–7 mils) which serves to keep the wire *A* taut. Finally this spring is connected to a heavy tungsten (60 mil) lead sealed through the ground-in Pyrex head *G*. This head was carefully ground into the 3° taper machined on to the end of the brass tube *B* and waxed into it—during final assembly—by means of a thin film of de Khotinsky cement. The fitted joint was covered in turn with a film of gum sandarac to prevent penetration of the thermostat oil. The gases were led into the gauge by means of the 1–2 mm Pyrex capillary tube *H* which was fused to the head *G*. Heavy copper wires (No. 18 B & S gauge) connected to the tungsten lead-in

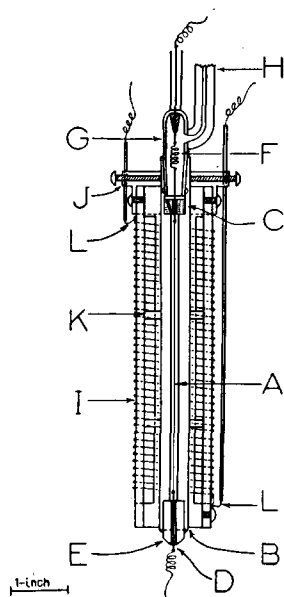


FIG. 1.

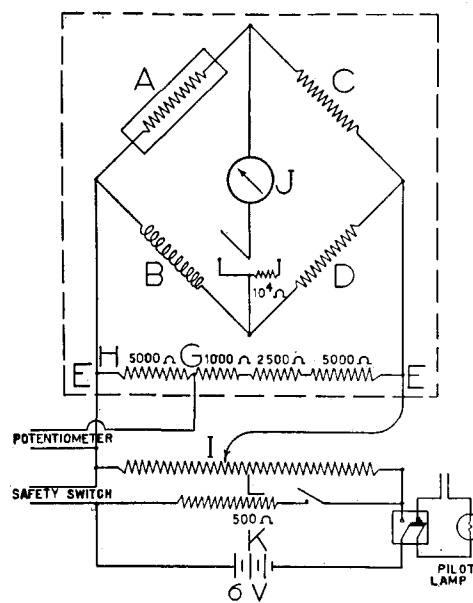


FIG. 2.

on the head and the platinum lead at the bottom served to make electrical connections to the gauge. All internal connections in the gauge were carefully brazed.

Concentrically about the gauge tube *B* was rigidly fastened a fiber or Catalin⁷ frame *I*. This frame is of $\frac{3}{4}$ -inch internal diameter, 6 inches long and is threaded symmetrically over 5 inches of its surface with a 28 standard thread. Six $5 \times \frac{3}{8}$ -inch slots were cut into it longitudinally to allow free passage of the oil through it to the gauge within. The whole frame was supported by means of a flanged brass collar *J* and its three set screws, as well as by the two thin brass spacers *K* ($\frac{1}{8}$ inch thick and soldered to the gauge tube *B*) machined so that the frame just slipped over them. On the threaded portion of this frame were *tightly* wound about 30 feet of (No. 36 B & S gauge) pure platinum wire the ends of which were securely fastened by means of tiny set screws and to which were soldered two heavier copper wires *L* (No. 28 B & S gauge) for electrical connections. The whole was carefully insulated from the gauge tube *B* and its connecting wires. As will be evident later, the

⁷ Blank tubes of Catalin may be obtained from the American Catalin Corporation, New York. Fiber is not especially recommended for this purpose because of poor machining qualities and a tendency to shrink when submerged in oil.

compensator winding should be made of as heavy a gauge platinum wire as practical to compact winding. In no case should it be made of much lighter gauge than that suggested above inasmuch as it is essential to proper operation of the gauge that this winding remain at the thermostat temperature and suffer as little heating due to the current flow as possible. This condition is more closely attained by exposing the wires of the winding as much as possible to free flow of oil around them, hence the grid-like form of the supporting frame.

The electrical circuit used is given in Fig. 2, the dynamic portion enclosed within the dotted lines being immersed beneath the thermostat oil (kerosene). This oil was carefully dried and purified by treatment with activated charcoal. All connections were heavily soldered and the entire dynamic part of the circuit, by being immersed beneath the thermostat oil, was held quite constant in characteristics while at the same time annoying variations due to parasitic currents were eliminated. *A* indicates the gauge, *B* the compensator, *C* and *D* two bare manganin (No. 22 B & S gauge) wound balancing resistors fully exposed to the thermostat oil but mounted on a Bakelite panel and finally the voltage dividing resistors *E* and *E*. These latter were made of a suitable combination of No. 231 type Shallcross *wire wound* 10 watt resistors mounted rigidly on a Bakelite frame. At points *G* and *H* was connected a good potentiometer—such as the Leeds and Northrup type K—capable of reading up to 1.6 volts and accurate to five decimal places. A 2-volt storage cell of high capacity—such as the Willard type DH-5-1—was used to feed the potentiometer. *I* is a special voltage divider made by winding a length of bare manganin wire (No. 24 B & S gauge) equivalent to ~ 100 ohms (~ 110 feet) on a grooved (11 turns per inch) Catalin drum, $4\frac{1}{2}$ inches in diameter and 10 inches long, which was mounted on two heavy brass bearings so that the drum could be rotated smoothly. In order to insure good contact through these bearings the axles were allowed to project somewhat and laminated phosphor-bronze brushes installed between the bearing plates and the axle ends. The threaded or grooved section of the drum surface was 8 inches long. A small traveling wheel with a fine V groove on

its outer edge was mounted on a long brass axle. This served as the moving contact represented by the arrow on *I* in Fig. 2. The wheel axle was mounted on a heavy spring-brass support which served to keep the wheel pressed firmly against the wire on the drum. Rotation of the drum caused the contact wheel to travel along the drum wire. Occasional cleaning and light greasing with a dilute solution of vaseline in petroleum ether always resulted in positive contact between wire and contact wheel, an important detail in this work. The entire mechanism was mounted on a heavy Bakelite base $\frac{1}{2}$ -inch thick. The entire instrument was mounted inside a wooden case with a tight fitting removable cover. This protected the winding from dust and laboratory fumes which attack manganin wire. All moving contacts were avoided where possible and all connections heavily soldered. Where bearings could not be avoided they were made massive to insure low positive contact resistance. The manganin wire on the rotating drum had its ends soldered to the bearing plates at the drum ends. A fine vernier for rotating the drum at final adjustment proved of value. A scale was mounted along the contact wheel axle and another on the drum end so as to allow the contact wheel to be put at the approximate position before closing the main switch. This proved a great convenience in rapidly setting the voltage to the approximate value required and also served to protect the galvanometers, which nevertheless had high resistances put in their circuits for protection against unduly large currents. These latter were removed at final adjustment. The galvanometer *J* was a high sensitivity (12 microvolts per mm) *low* internal resistance (> 25 ohms) instrument. It was operated critically damped. Finally the whole circuit was fed from a high capacity six-volt storage cell *K*. It is important that this cell deliver a *steady voltage* under moderate current drain. In order to obtain a constant voltage from the storage cells it was found good practice to shunt them with a moderately high resistance *L* (~ 500 to 1000 ohms) when not in use during periods of analysis and for about one hour before measurements are begun. This bleeding process helps to maintain a very constant voltage during an entire days operation and certainly removed

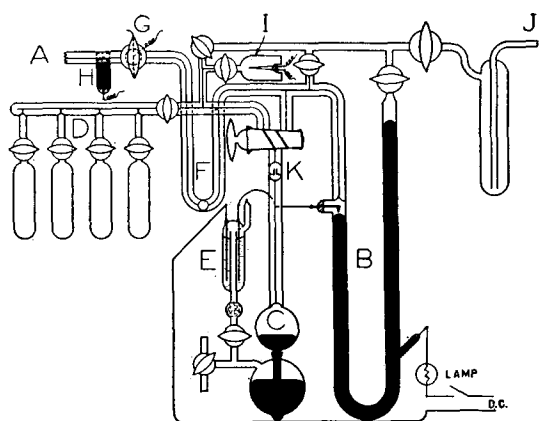


FIG. 3.

the initial drift on starting measurements, which proved very annoying. All the various parts in the Wheatstone bridge circuit should be very securely mounted within the thermostat bath. The suggestions given regarding the compensator design and construction especially should be followed.

The thermostat bath consisted of a tank about 12 in. \times 12 in. \times 14 in. equipped with a good stirrer located directly beneath the gauge so that the oil stream passed rapidly about the latter. When used in conjunction with a vacuum tube relay of the type described by Heisig and Gernes⁸ no difficulty was found in holding the bath temperature to better than 0.001°, provided the stirring was sufficiently *rapid* and *constant*. The bath temperature was adjusted so as to be about 3° above average laboratory conditions—26.35°C in our case—and heating was provided by means of a 40-watt electric light bulb completely immersed in the oil.

The thermostat used should be one which operates with the smallest possible heating and cooling cycles since their magnitude to a large degree determines the attainable precision of the gauge. The absolute temperature is of very much less importance as will be seen later from temperature coefficient data. The reason for this appears to be twofold. First, because of the practical impossibility of obtaining platinum wires for both the gauge and compensator of the same temperature coefficients of resistivity—

in our case they differed by 7 percent—and second because of the inevitable thermal lag between gauge tube and compensator. The entire set-up was entirely free from susceptibility to vigorous vibration or shock. This condition is not difficult to attain and is essential for successful operation.

The auxiliary apparatus for manipulation of the gases is shown in Fig. 3. In order that measurements could be carried out on as small an amount of gas sample as possible the dead space was kept as small as possible. To this end, all connections between the gauge *A* and its manometer *B* were made with 1–2 mm capillary tubing. The volume of gas necessary for our gauge was 4.3 cc S.T.P. The operation of the remainder of the apparatus is obvious. *C* is a small Toepler pump of \sim 100 cc capacity used to transfer the gas from the sampling tubes—attached to manifold *D*—to the gauge as well as for adjusting the gas pressure within the gauge. This adjustment was accurately and automatically attained by means of the electrolyzer *E*. The latter operated on a small current through the contacts sealed into the manometer at the desired positions. On turning on the current the electrolytic gas would slowly drive the mercury piston up until contact was broken at the desired pressure—about 200–230 mm. This method was highly satisfactory and gave reproducible results although our gauge readings were not excessively sensitive to pressure, as will be seen later from the pressure coefficient data of our gauge. The remainder of the apparatus consisted of a good high vacuum pumping system with a two-stage mercury vapor pump connected at *J*. The trap *F* served to exclude mercury and water vapors as well as other impurities from the gauge. Various refrigerants were used about it depending on the nature of the gas under investigation. *K* is a tiny grease trap.

Since it was found that *violent* overheating of the gauge wire resulted in serious disturbance of the thermal conductivity measurements and even in possible burn-out, it was considered good practice to introduce a safety switch mounted directly on the plug of stopcock *G*. This prevented pumping out the gauge with the gauge current on and thus possible serious overheating of the gauge wire due to evacuation

⁸ Heisig and Gernes, *Ind. and Eng. Chem., Anal. Ed.* **6**, 155 (1934).

of the gas from the gauge. The device consisted of a bent platinum wire, mounted to the back of the stopcock plug, which dipped into a pool of mercury *H* only when the stopcock was closed. Electrical connection was established by means of a phosphor bronze or silver "pig tail." It was placed directly in the main battery line and proved entirely satisfactory, always giving positive contact. The small tube *I* of about 20 cc capacity contained a small platinum filament which could be brought to a dull red glow by electrical heating. This served to equilibrate the hydrogen isotopes where that condition did not already exist in the gas samples. This, as we shall see later, was essential to correct analysis of the hydrogen isotopes. To measure the vacuum attained during pumping out, the thermal gauge was itself used as a vacuum gauge after calibration against a McLeod gauge. A pressure of $\sim 10^{-6}$ mm Hg was always required before analysis of a gas was undertaken. For this purpose a tapping key, shunted across the safety switch *G*, served to allow the gauge to be actuated during vacuum measurement. In assembling the gauge it was found good practice to glow the fine platinum wire in air for a short time, by means of a small gas flame, just before slipping it into place in the brass tube *B*. This process appears to remove all traces of oxidizable material from the wire surface and anneals away any strains introduced during drawing. It was found to introduce excellent stability characteristics to the wire. All the gauge parts were scrupulously cleaned of oil and grease before assembly.

ADJUSTMENT OF THE GAUGE CIRCUIT

To adjust the bridge circuit quickly, the following procedure was observed. Following assembly of the gauge, its internal resistance was measured at the thermostat temperature using a current so small that heating of the wire was negligible—this was found to be ~ 65 ohms for our gauge. Next, its internal resistance at a temperature $\sim 20^\circ$ higher was measured using a similar small current—this was found to be ~ 69.5 ohms for our gauge. The length of the compensator wire was now adjusted so that its total resistance at the thermostat temperature

about equaled that of the gauge at the same temperature. Finally the two manganin resistors *C* and *D* were wound and their respective resistances matched to those of the compensator and gauge—at the higher temperature—respectively, and placed in the appropriate arms of the bridge circuit. When this circuit was now brought to balance the gauge wire was heated to about 20° over the bath temperature, independent of the nature of the gas present around it. The voltage dividing resistors *E*–*E* were so selected that the tap-off to the potentiometer had about one-third of the total potential drop over the bridge, across it. Our combination consisted of 5000 ohms between points *F* and *H* and 8500 ohms between points *H* and *M*.

THEORY OF THE GAUGE

It is a well-known result of kinetic theory that the thermal conductivity of a gas for the condition that the mean free path of its molecules is small compared to the distance between the boundaries defining the temperature gradient is given by the Maxwell-Chapman-Enskog equation:

$$\lambda = \Lambda \frac{Cv}{M^{1/2} \sigma^2}, \quad (1)$$

where Λ is a constant of the particular system used, Cv the specific heat at constant volume, M the molecular weight and σ the molecular diameter. For a gas mixture of *i* species of molecules and assuming the thermal conductivities of each species to be independent of the presence of the other, Eq. (1) becomes:

$$\lambda = \sum_i \frac{Cv_i C_i}{M_i^{1/2} \sigma_i^2}, \quad (2)$$

where C_i is the mole fraction of the *i*th kind of molecule. The relative thermal conductivity of such a gas mixture to some standard reference gas 1 becomes then:

$$\frac{\lambda'}{\lambda} = \sum_i \left(\frac{Cv_i C_i}{M_i^{1/2} \sigma_i^2} \bigg/ \frac{Cv_1}{M_1^{1/2} \sigma_1^2} \right). \quad (3)$$

If I' and I_1 are the respective currents through the gauge wire to establish a given temperature

gradient in the gauge when the gases i and 1 are present and if r is the resistance of the wire under these conditions then since $\lambda = i^2 r \Delta$ it follows that Eq. (3) becomes

$$\frac{(I')^2}{I_1^2} = \left(\sum_i \frac{Cv_i C_i}{M_1^{\frac{1}{2}} \sigma_i^2} / \frac{Cv_1}{M_1^{\frac{1}{2}} \sigma_1^2} \right) = \frac{(E')^2}{E^2} = (R')^2. \quad (4)$$

E' and E_1 are the respective voltages across the whole Wheatstone diamond necessary to produce balance with the respective gases and obviously $I \propto E$. For the special case of the thermal conductivities of isotopic molecules Eq. (4) can be further simplified since it has been found⁹ that their molecular diameters are identical. It has been assumed that this condition holds for all cases of isotopic molecules. From Eq. (4) we see that the ratio $R' = E'/E_1$ should be independent of the condition of the wire, the bath temperature—provided that C_v is independent of the temperature—and independent of the total pressure used—again provided that C_v is independent of the pressure. Actually the value of R' is found only to approximate these conditions due, in part, to failure to meet the above provisions and due to the presence of unknown amounts of heating in the compensator winding and convection currents in the gauge itself. Thus, for precise results, the gauge must be calibrated with samples of known concentrations.

THE HYDROGENS

In the case of the hydrogen isotopes certain special conditions obtain which permit Eq. (4) to be amplified. If we define a quantity $p = D/H + D$, where D equals the number of atoms of deuterium per unit volume and H is the corresponding quantity for protium then p is the atom fraction of D in the gas, and if, further, we assume that the equilibrium $H_2 + D_2 \rightleftharpoons 2HD$ has been established at temperatures sufficiently high that the equilibrium constant $K = 4$ then it easily follows

⁹ Van Cleave and Maass have shown by viscosity and thermal conductivity measurements that σ_{D_2} and σ_{H_2} cannot be very different and so we considered

$$\sigma_{H_2} = \sigma_{HD} = \sigma_{D_2}.$$

Van Cleave and Maass, Can. J. Research 12, 57 (1935); *ibid.* 12, 372 (1935).

that the relations,

$$\begin{aligned} C_{H_2} &= (1-p)^2, \\ C_{HD} &= 2p - 2p^2, \\ C_{D_2} &= p^2, \end{aligned} \quad (5)$$

are satisfied. C is the mole fraction.

In addition, at 300°K, the values of $C_{v_{D_2}}$ and $C_{v_{HD}}$ are identical and equal to 4.989 while $C_{v_{H_2}}$ is 4.908 so that Eq. (4) becomes

$$R_p^2 = \frac{E_p^2}{E_{H_2}^2} = \frac{\frac{0.983}{M_{H_2}^{\frac{1}{2}}} (1-p)^2 + \frac{(2p-2p^2)}{M_{HD}^{\frac{1}{2}}} + \frac{p^2}{M_{D_2}^{\frac{1}{2}}}}{0.983/M_{H_2}^{\frac{1}{2}}}, \quad (6)$$

a form very similar to that arrived at by Sachsse and Bratzler² for their gauge. For mixtures of H_2 and D_2 this equation would become

$$R^2 = \frac{E_p^2}{E_{H_2}^2} = \frac{\frac{0.983}{M_{H_2}^{\frac{1}{2}}} (1-p) + \frac{p}{M_{D_2}^{\frac{1}{2}}}}{0.983/M_{H_2}^{\frac{1}{2}}}. \quad (7)$$

OPERATION OF THE GAUGE

After setting up the gauge and its auxiliary apparatus the whole system was thoroughly outgassed for twenty-four hours and the vacuum followed from time to time, liquid air being used on the trap F . When constant over a period of time the system was ready for measurement. A few cubic centimeters of carefully purified hydrogen were withdrawn from a storage bulb by means of the Toepler and *slowly* introduced into the gauge through the liquid-air trap until the manometer cuts off. The gauge stopcock was then closed and the drum voltage divider I rotated until balance was obtained. Readings on the potentiometer were now taken until constancy was obtained, usually within one minute after the current was turned on. In general the first determination after the gauge has been standing was not very reliable and consequently served only as an orientation result. When not in use the best practice was found to be to leave the gauge under vacuum. In working with other gases it was found best to use the pure light isotopic compound as the standard substance for checking the condition of the wire. Thus, in the case of heavy hydrogen analysis, light hydrogen was used as the standard substance while, for

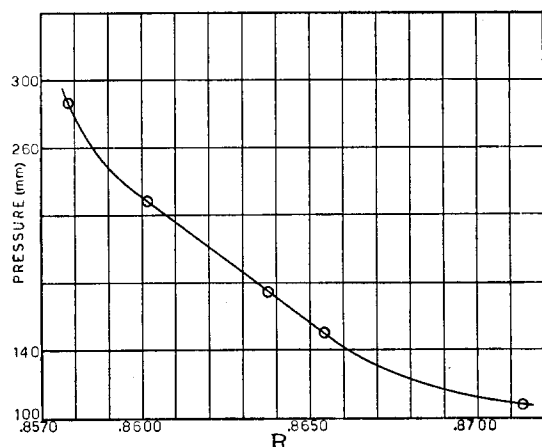


FIG. 4.

analysis of the methanes, CH_4 was the standard substance. Such procedure was found to yield the highest precision. Of course, only gases of the highest purity should be used. The hydrogens used were prepared by electrolysis from caustic soda solutions using platinum electrodes in an all glass system, traces of oxygen being removed by slow passage over a long glowing platinum filament and water by slow passage through a glass wool packed liquid-air trap.

CHARACTERISTICS OF THE GAUGE

The gauge was found to possess excellent stability during operation and seemed quite free from poisoning effects. Exposure to air or oxygen was found to be without any deleterious influence on the wire and reproducible values of R could be obtained immediately after exposure to them. Even accidental mild overheating of the wire or complete replacement of the wire by a new one left R essentially unchanged although the absolute values of E_{H_2} and E_{D_2} were markedly changed. This proved a very desirable property, for although the values of E_{H_2} and E_{D_2} were subject to slow drifts—over several days time—the values of R proved quite reproducible. In anticipation one might point out that these characteristics were found to hold for all the gases studied, including CH_4 , C_2H_6 and C_3H_8 . Thus for one platinum wire the value of R between a given pair of samples of H_2 and D_2 was found to be 0.85962. After overheating the wire this value was found to be 0.86014. On replacing

the wire by a new one a value of 0.85948 was found for R . During a series of measurements with H_2 over a period of eight hours the absolute value of E_{H_2} was found to vary by less than 0.1 of a millivolt.

The pressure and temperature dependences of the gauge are given in Fig. 4 and Table I, respectively. It will be noted that over the small range of temperatures studied the value of R is a good constant as anticipated by theory. However, R has a pressure dependence due in part to the differential heating effect in the compensator and in part to changes in the convective losses. This dependence is not large, however, and introduces no operational difficulties. It may be further reduced by a heavier compensator winding. It will be noted that the gauge was operated on the linear range of the curve in Fig. 4. In this range the pressure dependence of R was -6.8 units of spread per millimeter. Since the composition dependence of R was about -14.3 units of spread per percent deuterium one sees that to obtain an accuracy of 0.1 percent the pressure must be adjusted to 0.21 mm. This is easily attained with the method used.

CALIBRATION OF THE GAUGE

In order to calibrate the gauge for the hydrogen isotopes, equilibrated samples of known atom percent of deuterium were prepared by electrolysis of 17 cc of a 2 percent solution of caustic soda in about 50 percent D_2O using platinum electrodes. As the water electrolyzed away, samples (~ 200 cc) of the hydrogen gas were taken from time to time and analyzed for their D content by means of a quartz fiber gas density balance to be described elsewhere.¹⁰ These values were accurate to ± 0.1 percent. The unequilibrated samples were made synthetically by mixing known

TABLE I. The temperature dependence. Pressure of gas = 229 mm Hg.

THERMOSTAT TEMPERATURE °C	E_{D_2} (volts)	E_{H_2} (volts)	R
24.00	1.28900	1.50115	0.85868
25.00	1.29389	1.50712	0.85852
26.00	1.29872	1.51302	0.85846
26.32	1.30007	1.51425	0.85856

¹⁰ Trenner, J. Am. Chem. Soc. forthcoming paper.

amounts of pure H_2 and D_2 of ~ 99 percent purity.¹¹ The R values of these mixtures were determined directly and again after bringing them to equilibrium in the platinum wire equilibrator. These latter R values served to determine their precise D atom concentration from the calibration curve for equilibrated gases previously determined. These data are graphed in Fig. 5.

It will be noted that the change in the thermal conductivity on equilibration of the mechanical mixtures is small. This is due to the fact that, since the specific heats of all the molecular species involved are practically identical under our conditions, the only difference arises from the failure of the proportion $\sqrt{2} : \sqrt{3} = \sqrt{3} : \sqrt{4}$ to be true of the mass terms. Thus the production of $2HD$ from H_2 and D_2 results in a gas of slightly higher conductivity. Despite the smallness of the change in R which occurs on equilibration—even of a 50 percent mixture of D_2 and H_2 —an accuracy of 2–3 percent is attainable which, for some kinetic studies, would be adequate. Thus rates of approach to equilibrium of the hydrogen isotopes could be studied using this gauge.

In order to fit Eq. (6) to the observed data of the equilibrated gases it was found necessary to introduce three coefficients— α_{H_2} , α_{HD} and α_{D_2} —before each of the terms, respectively. A partial justification for this arises from the value of R obtained for pure D_2 (by short extrapolation of the calibration curve). The best value was found to be 0.8568 which when put into the equation

$$\alpha_{D_2} = \frac{\alpha_{H_2} R D_2^2 C_{v_{H_2}} M_{D_2}^{\frac{1}{2}}}{C_{v_{D_2}} M_{H_2}^{\frac{1}{2}}}$$

along with the appropriate values of the other terms and $\alpha_{H_2}=1$, gives $\alpha_{D_2}=1.022$. This correction coefficient arises from a small differential heating effect in the compensator winding as well as from the inevitable presence of differential convection losses. The former error can be minimized by heavier winding on the compensator, the latter by the use of baffles in the conductivity tube, and by horizontal instead of vertical mounting of the whole gauge. Using this value of α_{D_2} and $\alpha_{H_2}=1$ we now fit the equation:

¹¹ The author wishes to express his indebtedness to Mr. E. A. Smith of this laboratory for the preparation of these samples.

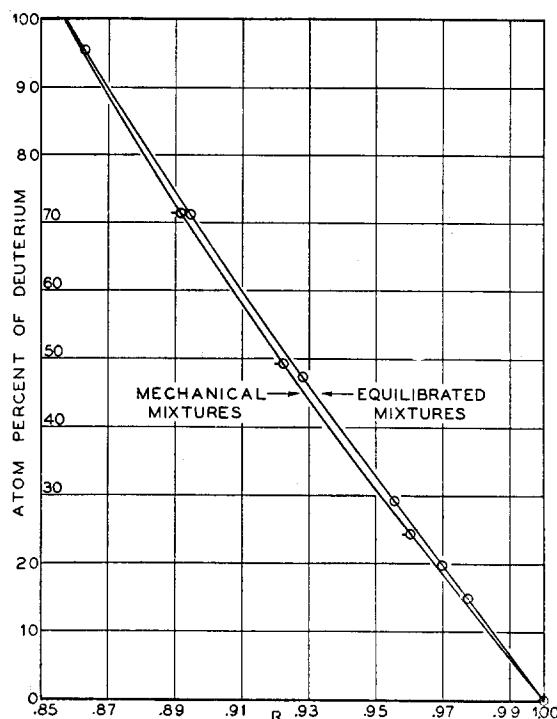


FIG. 5. Calibration curve for the hydrogen isotopes. Temperature = 26.35°C. Pressure = 229 mm Hg.

$$R_p^2 = \frac{[\alpha_{H_2}(0.983/M_{H_2}^{\frac{1}{2}})(1-p)^2 + \alpha_{HD}((2p-2p^2)/M_{HD}^{\frac{1}{2}}) + \alpha_{D_2}(p^2/M_{D_2}^{\frac{1}{2}})]/[0.983/M_{H_2}^{\frac{1}{2}}]}{(8)}$$

to the observed data by arbitrarily selecting the value of α_{HD} and using $C_{v_{D_2}}=4.987$, $C_{v_{H_2}}=4.908$, $C_{v_{HD}}=4.988$, $M_{H_2}=2.016$, $M_{HD}=3.022$, $M_{D_2}=4.029$. A value of $\alpha_{HD}=1.013$ was found to give the best fit. This fit is illustrated by the data given in Table II. On putting the numerical values in Eq. (8) it becomes on transposition:

$$p = \frac{0.5500 - 0.3025 - 0.6351(1-R^2)}{0.1837} \quad (9)$$

The maximum deviation between Eq. (9) and the observed data is 0.5 percent at the lower values of p and 0.2 percent at the higher values. Such agreement is sufficient for most work and since the gauge described is easy to reproduce—being entirely machined in its important parts—it should be possible to use Eq. (9) in those cases in which direct calibration is not possible, although the method of known synthetic mixtures is certainly more desirable and precise. In consideration of the results of direct calibration and

general reproducibility we consider our relative results accurate to somewhat better than 0.1 percent and the absolute values to ± 0.1 percent. Not more than ten minutes is required for a determination. If results of the highest possible precision are desired the unknown determination should be sandwiched between determinations on the standard substance so as to eliminate small errors due to the small drift of the wire characteristics. This is not necessary for average work, however.

ANALYSIS OF THE ISOTOPIC ALIPHATIC HYDROCARBONS. THE METHANES

Methane presented by far the most difficult purification problem. This is due to two causes. Firstly the spread of the thermal conductivities of CH_4 and CD_4 is not large due to an overlapping of the mass and specific heat effects thus making desirable, measurements of the highest precision and, in consequence, gas samples of the highest purity. Secondly the high vapor pressure displayed by CH_4 and CD_4 at normal liquid-air temperatures made its fractionation from traces of the fixed gases such as O_2 , N_2 , H_2 , etc. rather difficult. Experience showed that the most reliable procedure to employ for the purification of the methanes was to use a special low temperature trap and to distill the sample into it at low pressures ~ 1 mm with continuous pumping and then subsequently to collect the purified sample by raising the trap temperature to normal liquid-air temperatures and Toeplering off into a sampling bulb. The details of this trap and the method of obtaining the necessary low temperatures have been described elsewhere.⁵ The method of preparation of the methanes used has also been fully described in another place.¹² The

methods employed for preparing the methane samples obtained from a reaction system prior to analysis of their C-D content is fully described elsewhere.¹³

The results given for the thermal conductivity of CH_4 were obtained by investigation of several samples and by successive purifications until check results were obtained. A similar procedure was employed with CD_4 except that, in addition, exhaustive deuterizations were first carried out on a nickel catalyst. After the final deuterization both the CD_4 and the hydrogens in equilibrium with it were analyzed. From a knowledge of the equilibrium constant

$$K = \frac{\text{C-D}}{\text{C-H}} \times \frac{\text{H}}{\text{D}}$$

previously determined by infrared analysis and found to be 1.8¹² and the value of H/D of the hydrogens, the value of C-D/C-H for the best CD_4 was estimated. This was found to be 98.0 percent C-D in good agreement with previous estimates made by infrared analysis.¹⁴ To obtain a calibration point on the curve, a known mixture of the two standardized samples of CH_4 and CD_4 was made up and its conductivity determined. Although this mixture was not brought to equilibrium, we feel that no great error was introduced—as would have occurred had this method been used with the hydrogen isotopes—because of the very small mass difference. The error introduced is certainly within the experimental error. In this way the calibration data for Fig. 6 were obtained.

The operation of the gauge was carried out in a manner entirely analogous to that employed for the hydrogens except that a solid carbon dioxide-acetone bath was substituted for liquid air around the gauge trap *F*. A carefully purified sample of CH_4 was used as the standard reference substance. Valuable gas samples could always be returned to their bulbs after analysis, by means of the Toepler pump, with very little loss and if condensable in liquid air with no loss at all. (Such procedure was always used when pure deuterio-

TABLE II.

R_p^2 (Observed)	$p \times 10^2$ (Observed)	$p \times 10^2$ (Calculated)
0.7349	100	100
0.7446	95.5	95.4
0.7999	71.4	71.2
0.8614	47.3	46.9
0.9131	29.2	28.7
0.9402	19.7	19.2
0.9553	14.8	14.2
1.0000	0	0

¹² Morikawa, Benedict and Taylor, J. Am. Chem. Soc. 58, 1445 (1936).

¹³ Morikawa and Trenner, Ind. Eng. Chem., Anal. Ed. forthcoming paper.

¹⁴ Benedict, Morikawa, Barnes and Taylor, J. Chem. Phys. 5, 1 (1937).

hydrocarbons were being worked with.) It will be observed that the curve is *not* linear as would be expected from Eq. (4) for this case. Furthermore the slope is positive pointing to the fact that the specific heat of CD_4 is greater than that of CH_4 and so completely overcomes the effect on the thermal conductance to be expected from the mass ratio alone. These effects were found to be true of all the isotopic isomers of the aliphatic hydrocarbons studied. The accuracy of analysis is only about 1 percent due to the relatively small spread.

THE ETHANES

The problem of the ethanes proved a much simpler one, inasmuch as purification was relatively easy and a method for direct preparation of an ethane of known intermediate composition was worked out. For the methods of purification used, reference should be made to the paper previously indicated.¹³ For the preparation of the standard intermediate ethane¹⁵ complete details are given in another publication¹⁶ and so will not be repeated here except to indicate that controlled deuterization of ethylene on a copper catalyst at low temperatures was the reaction employed. The purest C_2D_6 of known composition was obtained in an entirely analogous manner to that employed for obtaining CD_4 . The results of our calibration are shown in Fig. 6. An equilibrium constant

$$K = \frac{\text{C-D}}{\text{C-H}} \times \frac{\text{H}}{\text{D}} = 2.4$$

was used, estimated from results previously obtained.¹⁷ It will be noticed that they follow in general form those obtained from the methanes. The gauge operation was identical with that for the methanes. Due to the greater specific heat difference between C_2H_6 and C_2D_6 obtaining in this case over that for the methanes a larger spread results and a consequent *greater* analytical accuracy of at least 0.5 percent accrues.

¹⁵ Intermediate propanes can also be made in an analogous way.

¹⁶ Morikawa, Trenner and Taylor, J. Am. Chem. Soc. 5, 203 (1937).

¹⁷ Morikawa, Benedict and Taylor, J. Am. Chem. Soc. 58, 1795 (1936).

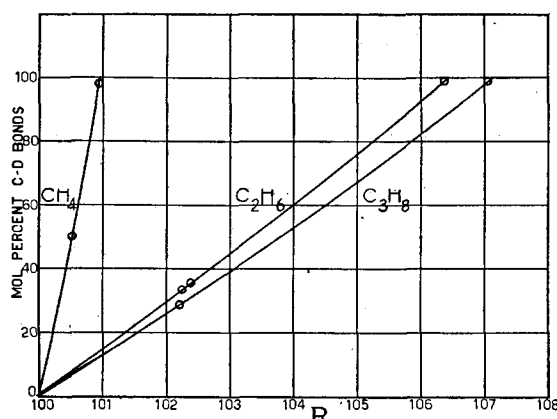


Fig. 6. Calibration curves for the isotopic isomers of the aliphatic hydrocarbons. Temperature = 26.35°C. Pressure = 229 mm Hg.

THE PROPANES

This substance presented an entirely analogous problem to that of ethane and thus the method of treatment was entirely parallel. The method of preparing the partially deuterized propane of known composition is fully described elsewhere¹⁶ as are the methods of purification.¹³ In operation of the gauge the only change made was the use of a -50° bath on trap *F*. The calibration results shown in Fig. 6 again parallel those obtained for the methanes and ethanes except that the specific heat difference is larger than either of the former as would be expected. The analytical accuracy increases apace and is better than 0.5 percent. The value of the equilibrium constant

$$K = \frac{\text{C-D}}{\text{C-H}} \times \frac{\text{H}}{\text{D}}$$

used was 2.34.¹⁶

ANALYSES ON OTHER GASES

At the present time only rough measurements have been made on the butanes and so no reliable data can be presented. However, these preliminary experiments indicate that no difficulties are encountered using a technique similar to that used on the lower hydrocarbons. The trap bath *F* must be raised to -25° for this work. Longer pumping periods are required due to the solubility of the butanes in the stopcock grease.

The ammonias have been investigated, and in this case it was found that the mass and specific heat effects almost cancel each other with the

result that the analytical spread is too small to permit sufficient accuracy to be attained. Obviously combinations of the gases studied in this research can be analyzed for by the thermal conductivity method described and several such analyses have been made by the author.¹³ It is planned to use this method of analysis in general on the isotopic isomers of neon, oxygen and carbon. Simple calculation shows that $C^{13}H_4$ and $C^{12}H_4$ could be determined with an accuracy of about 0.5 percent since in this case no marked specific heat differences appear possible. The important features which the compound to be used for thermal analysis must have are relatively small "dead" mass and either very large or

negligible specific heat differences for the isotopic isomers.

That this type of thermal conductivity gauge has proved a powerful tool in the investigation of a wide variety of researches concerned with the kinetics of general aliphatic hydrocarbons is amply indicated by several of the papers referred to above. Its most notable feature is its easy adaptation to carrying out analyses on *both* the hydrogens and the hydrocarbons permitting therefore a very complete study to be made of both the kinetics and the equilibria in any hydrogen isotope-lower aliphatic hydrocarbon system, provided only a correct separational procedure is adopted.

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On the Fundamental Frequencies of CH_2 , CHD , CD_2 , $CHCl$, $CDCl$, and *Cis* and *Trans* $C_2H_2D_2$ and $C_2H_2Cl_2$

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A valence force treatment of the groups CH_2 , CHD , CD_2 , $CHCl$, $CDCl$ is given. The relative dependence of the three fundamental frequencies calculated for each group on the deformation force constant is used as a guide in correlating these frequencies with the three individual modes of vibration of the group. On the basis of this calculation, an assignment of the fundamental frequencies of *cis*, *trans* and

asymmetric $C_2H_2D_2$ calculated by Manneback and Verleysen is given. Also from the data on the degrees of depolarization of the Raman lines of *cis* $C_2H_2Cl_2$ and *trans* $C_2H_2Cl_2$, intensity and selection rules in Raman effect and infrared absorption, an assignment of the fundamental frequencies of these isomers is suggested.

I. INTRODUCTION

THE molecules C_2H_4 , C_2D_4 , C_2Cl_4 belong to the symmetry type V_h , the *cis* $C_2H_2D_2$ or $C_2H_2Cl_2$ to the type C_{2v} , and the *trans* $C_2H_2D_2$ or $C_2H_2Cl_2$ to the type C_{2h} . Each molecule possesses twelve fundamental vibrations, nine of which take place in the plane of the molecule, and two in directions perpendicular to the plane. One is the torsional vibration. The symmetrical properties and the selection rules in the infrared and the Raman effect can be summarized in Table I.¹

In C_2H_4 , except for the torsional vibration which is inactive in both the infrared and the Raman effect, there is little doubt concerning the other eleven frequencies. These frequencies are given in Table II. For the vibrations S_1 and A_1 ,

Sutherland and Dennison² obtained a potential function with four constants. For the nine vibrations in the plane of the molecule, Bonner³ obtained a potential function containing eight constants, while Manneback and Verleysen² determined one with eleven constants. With this potential function and on the assumption that it is invariant under a substitution by an isotope, Manneback and Verleysen calculated the nine frequencies of the vibrations in the molecular plane of each of the *cis*, *trans* and asymmetric $C_2H_2D_2$. The determinantal equation in each case separates into two; one of the 5th degree for the five π' , S , π vibrations in the case of the *cis*, *trans* and asymmetric $C_2H_2D_2$, respectively, and one

¹ See, for example, Placzek, *Leipziger Vorträge* (1931).

² G. Sutherland and D. M. Dennison, Proc. Roy. Soc. A148, 250 (1935).

³ Bonner, J. Am. Chem. Soc. 58, 34 (1936).