SUMMARY

An account is given of the Raman spectra of the following metallic alkyls : zinc dimethyl and diethyl, mercury dimethyl and diethyl, bismuth trimethyl, tin tetramethyl and lead tetraethyl. The Raman frequencies are discussed in relation to the structure of the molecules. It is found that the dialkyls may be treated as symmetrical non-linear triatomic molecules of the type XY_2, in which the metallic atom X has a large valency angle. Bismuth trimethyl conforms to a pyramidal model, while the tetra-alkyls have a regular tetrahedral structure.

The Effect of Temperature on the Thermal Conductivity and the Accommodation Coefficient of Hydrogen

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INTRODUCTION

Comparatively little work has been attempted on the subject of the effect of temperature on the conduction of heat through hydrogen.

Eucken*† carried out investigations on the thermal conductivity of hydrogen for a range of temperature between $-252 \cdot 2°$ and 100° C. A modification of the hot wire method was employed in which his final values were obtained relative to a predetermined value for the thermal conductivity of air, viz., 566×10^{-7} cal cm^{-1} sec^{-1} deg^{-1}. The values thus determined at various temperatures are given in Table I and compared with those of other observers.

All methods which have been used to investigate the heat conduction through gases, with one exception, are complicated by the existence of the errors due to convective losses or mass motions of the gas itself. Although these mass motions are diminished to a great extent by decreasing the gas pressure, this procedure restricts the measurements to a gas in

* 'Phys. Z.,' vol. 14, p. 324 (1913).
† 'Phys. Z.,' vol. 12, p. 1101 (1911).

more or less a state of rarefaction and at the same time—in particular in the hot wire method—the troublesome temperature drop effect is enhanced by reason of the low pressure and also by the extremely small dimensions of the wires used. Further, the calculation of the convective losses has not yet been found theoretically possible.

TABLE I

Temperature	K × 10^7	Observer
−252·2	322	Eucken*
−191·5	1324	
0	3970	
−191·5	1331	Eucken†
−182·6	1481	
−78·4	3065	
0	3960	
100	4994	
0	4165	Weber, S.‡
0	4100	Schleiermacher§
100	5228	
0	4190	Schneider‖
0	4180	Schneider¶

* 'Phys. Z.,' vol. 12, p. 1101 (1911).
† 'Phys. Z.,' vol. 14, p, 324 (1913).
‡ 'Ann. Physik,' vol. 54, p. 437 (1917).
§ 'Wied. Ann.,' vol. 34, p. 623 (1888).
‖ 'Ann. Physik,' vol. 79, p. 177 (1926).
¶ 'Ann. Physik,' vol. 80, p. 215 (1926).

The problem of disentangling experimentally the convective losses from those due to pure conduction was the subject of an investigation by Gregory and Archer.** This was effected by the use of a double system of tubes and wires which in conjunction with the bridge system used enabled them to eliminate experimentally these losses from their measurements. This and other investigations which have since been carried out by other observers have firmly substantiated the truth of their arguments in this respect. It is emphasized that the success in this instance was due to the important modification imposed on the hot wire method in which an electrically heated wire is maintained at constant temperature to a high degree of accuracy while the pressure of the gas is lowered by successive amounts, a procedure only possible with a bridge

** 'Proc. Roy. Soc.,' A, vol. 110, p. 91 (1926).

system and not with a potentiometer method as adopted by Weber* and other observers in their researches on the subject.

Theory of Method

Kundt and Warburg,† who were led to predict, by analogy with the "slip" effect in viscosity, the existence of a temperature discontinuity at the surface of separation of a heated solid and a gas, defined such temperature drop by the relation

$$\delta\theta = -\mu \frac{d\theta}{dn}, \tag{1}$$

where $d\theta/dn$ represents the normal temperature gradient at a point on the solid, and μ a quantity which was found to be proportional to the mean free path of the gas molecules.

More recently the subject has been developed along theoretical lines by Smoluchowski‡ who, making use of Maxwell's§ hypothesis that molecules can be regarded as centres of forces of repulsion varying inversely as the fifth power of the distance of separation, found the temperature drop to be represented by the relation

$$\begin{aligned}\delta\theta &= -\gamma\lambda \frac{d\theta}{dn}\\ &= -\frac{15}{2\pi}\frac{2-a}{2a}\lambda\frac{d\theta}{dn},\end{aligned} \tag{2}$$

where a is the accommodation coefficient as defined by Knudsen,‖ λ the mean free path of the gas molecules and $d\theta/dn$ the normal temperature gradient at a point in the gas near the heated surface.

A second calculation of $\delta\theta$ by Smoluchowski¶ was based on a hypothesis, also used by Maxwell in his theoretical investigation of "slip" in gases, in which it was assumed that amongst all molecules striking a surface only a fraction β attain thermal equilibrium, while the remainder $(1 - \beta)$ are reflected without change of temperature. These two aspects give results which are indistinguishable from one another in their application to experimental practice. Equation (1) applies only to small tempera-

* 'Ann. Physik,' vol. 54, p. 437 (1917).
† 'Pogg. Ann.,' vol. 156, p. 177 (1875).
‡ 'Ann. Physik,' vol. 35, p. 983 (1911).
§ 'Phil. Trans.,' vol. 170, p. 231 (1879).
‖ 'Ann. Physik,' vol. 34, p. 593 (1911).
¶ 'Ann. Physik,' vol. 35, p. 983 (1911).

ture discontinuities and to heat transfer between surfaces where the curvature is large compared with the mean free path.

If T_1 and T_2 represent the temperatures of the wire and the internal surface of the tube when thermal equilibrium is attained, and if T''_1 and T'_1 denote the average temperatures of the molecules approaching and leaving the wire, fig. 1, then $T_1 - T''_1$ is termed the temperature drop at the wire and $T''_2 - T_2$ the corresponding discontinuity of temperature at the wall of the tube. The average temperature of the molecules leaving the wire will depend on the extent to which the impinging molecules accommodate themselves with the temperature of the wire.

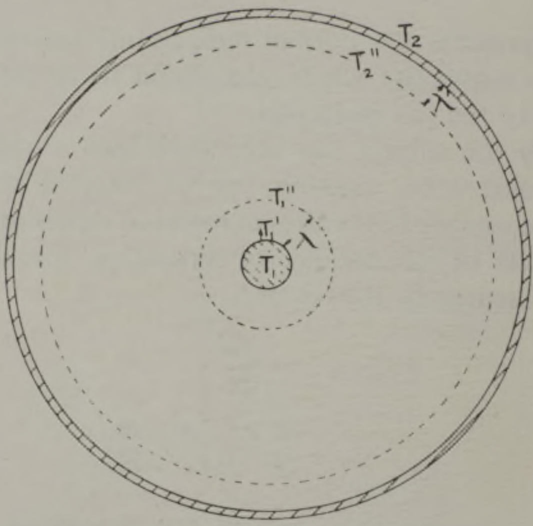

Fig. 1

Knudsen* has defined such an effect in terms of the mean energies of the approaching and receding molecules. If E_1, E'_1 and E''_1 are the mean energies of the molecules at the temperatures T_1, T'_1 and T''_1 respectively, then

$$\frac{E'_1 - E''_1}{E_1 - E''_1} = \text{constant} = a, \tag{3}$$

where a is known as the accommodation constant.

If the velocity distribution of the molecules leaving the wire corresponds to a Maxwellian distribution, then equation (3) can be written

$$a = \frac{E'_1 - E''_1}{E_1 - E''_1} = \frac{T'_1 - T''_1}{T_1 - T''_1}, \tag{4}$$

* 'Ann. Physik,' vol. 34, p. 593 (1911).

If, however, a Maxwellian distribution does not exist, equation (4) no longer holds in respect of the emitted molecules. On this account, Langmuir and Blodgett* in their investigation of the effect of temperature on the accommodation constant of hydrogen have avoided Knudsen's definition of a.

For a cylindrical temperature distribution, as in the hot wire method, the equation expressing thermal equilibrium in the absence of convection can be written in the form

$$\begin{aligned} Q \log \frac{r_2 - \lambda'}{r_1 + \lambda} &= 2\pi K l \, (T''_1 - T''_2) \\ &= 2\pi K l \, (T_1 - \delta\theta_1 - \overline{T_2 + \delta\theta_2}) \\ &= 2\pi K l \, (T_1 - T_2 - \delta\theta_1 - \delta\theta_2), \end{aligned} \tag{5}$$

where T_1 and T_2 are the wire and wall temperatures, $\delta\theta_1$ and $\delta\theta_2$ the temperatre drop at the wire and the wall respectively, λ and λ' the mean free paths corresponding to the temperatures of the wire and the wall, r_1 and r_2 the radii of the wire and internal tube wall and K the absolute thermal conductivity at a mean temperature across the gas layer. Q represents the heat transfer per second, corrected for radiation, from a wire of length l whose temperature, from consideration of the principle of compensation, is considered constant throughout its length, a point fully discussed in previous papers.

From (2) above

$$\delta\theta_1 = \frac{\lambda_0 P_0}{P} \frac{15}{2\pi} \frac{2 - a}{2a} \frac{Q_0}{2\pi K_1 l r_1} \tag{6}$$

and

$$\delta\theta_2 = \frac{\lambda'_0 P_0}{P} \frac{15}{2\pi} \frac{2 - a'}{2a'} \frac{Q_0}{2\pi K_2 l r_2}, \tag{7}$$

where P_0 denotes a pressure of 1 atmosphere in cm of mercury and P the existing gas pressure in the tubes measured in the same units, λ_0 and λ'_0 the mean free paths of the gas molecules at atmospheric pressure and at the temperatures of the wire and wall respectively. The accommodation constants a and a' will differ slightly by reason of the different temperatures of the wire and internal wall surface. Q_0 represents the heat transfer operative in the absence of temperature drop and convection, K_1 and K_2 the absolute thermal conductivity of the gas at the wire and wall temperatures.

* 'Phys. Rev.,' vol. 40, p. 78 (1932).

Substituting (6) and (7) in (5)

$$\mathrm{Q}\log\frac{r_2-\lambda'}{r_1+\lambda} = 2\pi\mathrm{K}l\,(\mathrm{T}_1-\mathrm{T}_2) - 2\pi\mathrm{K}l\,(\delta\theta_1+\delta\theta_2)$$

$$= 2\pi\mathrm{K}l\theta - \frac{15}{2\pi}\frac{2\pi\mathrm{K}l\mathrm{P}_0}{\mathrm{P}}\frac{\mathrm{Q}_0}{2\pi l}\left(\frac{2-a}{2a}\frac{\lambda_0}{\mathrm{K}_1 r_1} + \frac{2-a'}{2a'}\frac{\lambda'_0}{\mathrm{K}_2 r_2}\right). \qquad (8)$$

Since the ratio of $r_2 : r_1$ is of the order of 250 : 1 in the present instance, the term

$$\frac{2-a'}{2a'}\frac{\lambda'_0}{\mathrm{K}_2 r_2}$$

is small compared with

$$\frac{2-a}{2a}\frac{\lambda_0}{\mathrm{K}_1 r_1}$$

and also since a' will differ only slightly from a on account of the small variation of a with temperature, it is sufficiently exact to write a for a' in (8) and hence

$$\frac{\mathrm{Q}}{\theta}\log\frac{r_2-\lambda'}{r_1+\lambda} = 2\pi\mathrm{K}l - \frac{15}{2\pi}\frac{2-a}{2a}\frac{\mathrm{P}_0}{\mathrm{P}\theta}\frac{2\pi\mathrm{K}l\mathrm{Q}_0}{2\pi l}\left(\frac{\lambda_0}{\mathrm{K}_1 r_1} + \frac{\lambda'_0}{\mathrm{K}_2 r_2}\right). \qquad (9)$$

For reasons considered below, θ, the temperature difference between the wire and the wall, will vary progressively with time during the course of the experiment.

Since

$$\mathrm{Q}_0 = \frac{2\pi\mathrm{K}l\theta}{\log\dfrac{r_2}{r_1}},$$

equation (9) can be written

$$\frac{\mathrm{Q}}{\theta}\log\frac{r_2-\lambda'}{r_1+\lambda} = 2\pi\mathrm{K}l - \frac{\mathrm{I}^2}{\log\dfrac{r_2}{r_1}}\frac{15}{2\pi}\frac{\mathrm{P}_0}{\mathrm{P}}\frac{2-a}{2a}\left(\frac{\lambda_0}{\mathrm{K}_1 r_1} + \frac{\lambda'_0}{\mathrm{K}_2 r_2}\right), \qquad (10)$$

where $\mathrm{I} = 2\pi\mathrm{K}l$.

A linear relation therefore holds between

$$\frac{\mathrm{Q}}{\theta}\log\frac{r_2-\lambda'}{r_1+\lambda} \quad \text{and} \quad \frac{1}{\mathrm{P}},$$

the intercept value of which corresponds to the term $2\pi Kl = I$, from which the absolute conductivity of the gas corresponding to an average temperature $\frac{T_1 + T_2}{2}$ can be calculated.

The slope of the line is a measure of the quantity

$$\frac{I^2}{\log \frac{r_2}{r_1}} \frac{15}{2\pi} P_0 \frac{2-a}{2a} \left(\frac{\lambda_0}{K_1 r_1} + \frac{\lambda'_0}{K_2 r_2}\right),$$

from which a at the temperature of the wire is determined

The values of λ_0 and λ'_0 at their appropriate temperatures are calculable in terms of viscosity data.

Equation (10) would appear to require a correction to allow for the variations of K with possible variations in T_2 the wall temperature, since K corresponds to the average temperature $\frac{T_1 + T_2}{2}$, T_1 being constant. If it be supposed that observations commence when the wire and internal wall temperatures are T_1 and T_2, the correcting factor is $1 \pm \alpha . \delta\theta$, where $\delta\theta$ represents a maximum alteration in T_2 during the time of the experiment and the maximum possible change in K is given by

$$K \pm \delta K = K(1 \pm \alpha . \delta\theta),$$

α being the temperature coefficient of change of thermal conductivity. α for a large range of temperature is of the order 0·003 and therefore the factor $1 \pm \alpha . \delta\theta$ is of negligible effect for possible variations of wall temperature of 0·5°, which was the maximum change of temperature permitted during the total time occupied in the observations.

The quantities K_1 and K_2 corresponding to the wire and wall temperatures will differ by an amount of the order of 5% in the present experiments and a further modification of the working equation (10) is possible, since the magnitude of the terms $\lambda'_0/K_2 r_2$ and $\lambda_0/K_1 r_1$ are in the ratio of 1 : 250 approximately. Hence, to this order of accuracy, we can write $K_1 = K_2$ and the relation reduces to

$$\frac{Q}{\theta} \log \frac{r_2 - \lambda'}{r_1 + \lambda} = \frac{Q}{\theta} \log \frac{r_2}{r_1} \left(\frac{P - \frac{\lambda'_0 P_0}{r_2}}{P + \frac{\lambda_0 P_0}{r_1}} \right)$$

$$= 2\pi Kl - \frac{15}{2\pi} \frac{P_0}{P} \frac{2-a}{2a} \frac{I}{\log \frac{r_2}{r_1}} \frac{K}{K_1} \left(\frac{\lambda_0}{r_1} + \frac{\lambda'_0}{r_2}\right). \qquad (11)$$

In actual practice, the existence of a uniformly heated wire can be realized by means of the compensating device used by Gregory and Archer* in the earlier experiments on the subject. The system adopted in the present investigation consisted of two similarly constructed tubes and wires, dimensionally the same, except in length and disposed in opposite arms of a Callendar and Griffiths bridge. It has been shown from theoretical considerations by Gregory and Archer† in a previous paper, that the resistance associated with such a balanced bridge system is that corresponding to a wire equal in length to the difference between the main and compensating wires, and which is uniform in temperature throughout its length, provided the design of the tube system is such that the quantities

$$e^{-2l_1\sqrt{P}} \quad \text{and} \quad e^{-2l_2\sqrt{P}}$$

are negligibly small compared with unity, where $2l_1$ and $2l_2$ are the lengths of the main and compensating wires and P a quantity depending on the dimensions of the system and the heat losses from the surfaces of the wires.

When such conditions are satisfied, the system is termed to be compensating in that the temperature distribution along each of the two wires is the same and the heat losses by conduction through the leading wires connected to each of the two wires are equal.

In addition to the effects considered above, two others are of especial consequence as associated with the present experimental procedure. As an example of one of these effects, the case is considered of a tube system when immersed in the vapour of a boiling liquid. In this instance a failure of attainment of the stationary state was observed, and was found to be directly due to a progressive accumulation of heat on the tube wall, which, if the internal wire is maintained at a constant temperature, leads to a steadily decreasing temperature difference between the wire and wall, and the latter, being at a higher temperature than the vapour, a large error is possible in the calculated thermal conductivity of the gas, if equality of the wall and vapour temperatures is assumed. The existence of such an effect first led the author to consider the advantage of directly measuring the temperature of the external surface of the tube by fusing platinum wire to the surface. The procedure of covering the wire with a thin coating of pyrex glass, and then fusing the same to the tube wall, was found to be satisfactory. This is shown diagrammatically in fig. 2.

* 'Proc. Roy. Soc.,' A, vol. 110, p. 91 (1926).
† 'Phil. Mag.,' vol. 3, p. 931 (1927).

A series of experiments was undertaken to test the constancy of the wall temperature under the conditions associated with the use of the ice and water thermostat, designed by the author and used in conjunction with Mr. Archer in previous experiments, and also with a similar thermostat using oil at various temperatures over a range of some 300 degrees. In all cases, except that of the ice and water thermostat, a heating effect was found to exist and to be of greater magnitude for gases of high thermal conductivity.

Such an effect is specially noticeable with the present bridge system in which the heating current through the wires is raised or lowered in order to maintain constancy of the wire temperature. In every case the effect was accompanied by a lowering of the current strength which pointed to a progressive heating of the tube wall.

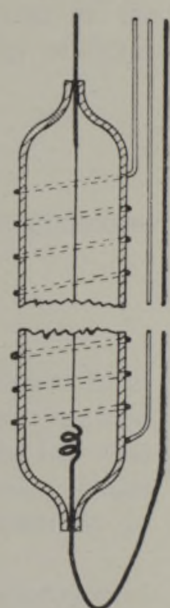

FIG. 2

The use of the oil thermostat was complicated by the difficulty of adjusting and maintaining a constant temperature throughout the mass of oil, which temperature was found to vary intermittently, however carefully the current through the heaters was adjusted. This was due to the uncertainty from time to time of the atmospheric conditions prevailing in the laboratory and external to the thermostat, and the sensitivity of the bridge used was such that it was found impossible to secure an exact balance for the current flowing through the hot wire system. The procedure was adopted of so adjusting the current through the heaters in the thermostat that the oil was allowed to cool at a rate sufficiently small to permit of accurate adjustment of the bridge current and at the same time, to overcome the heating effect referred to above. By this means the temperature of the wall surface could be caused to decrease sufficiently slowly with time to enable an accurate experimental procedure to be carried out, and in many instances a rate of decrease of less than $0 \cdot 5^{\circ}$ per hour was observed. The term "wall effect" has been introduced by the author to denote the resultant temperature change of the wall due to the two thermal effects considered above, such temperature changes being measured during the course of the experiments by the platinum thermometer in intimate fusion with the tube wall.

The thermostat was constructed of a welded steel inner vessel of 10 gallons capacity surrounded by an outer vessel also of steel, the intervening space being packed with slag wool. The inner vessel was fitted with a brass frame to which was bolted six 100-ohm heating coils con-

nected in parallel and disposed symmetrically as shown diagrammatically in fig. 3. The arrangement for producing turbulence in the thermostatic fluid consisted of an L-shaped tube open at both ends, the lower end carrying a bevel gear operated by a vertical driving shaft to which was attached a horizontal pulley driven by an electric motor. The other end of the bevel gear was in rigid connection with a propeller by which means the oil was drawn from the tank in the neighbourhood of the heaters and caused to flow along the vertical portion of the L-tube in which was fixed the tube system used in the experiments.

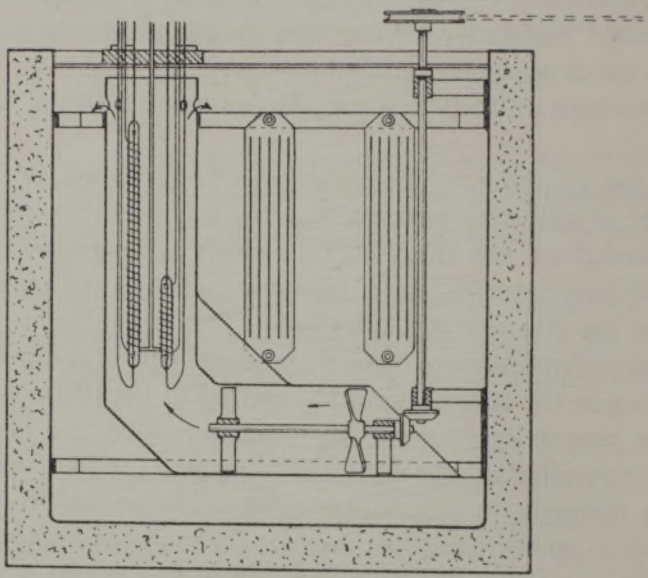

Fig. 3

It was found necessary during the course of the experiments to supplement the fixed heaters by the addition of another movable heater of about 2000 watts capacity. This was because of the large amount of heat required for the experiments in the neighbourhood of 300° C. The tank was closed by two steel half-plates covered by asbestos cement with an aperture through which the experimental system passed into the tank. The oil used was a thermostatic substance supplied by Messrs. C. C. Wakefield and Co., Ltd., and termed Special Thermostat Oil.

Wall Temperature Correction

An appreciable correction to the internal wall temperature was found necessary on account of the large thickness of the walls of the tubes employed.

If the temperatures of the internal and external surfaces are represented by T_2 and T_3, then T_2 can be found from the relation

$$T_2 = T_3 + \frac{Q \log \frac{r_3}{r_2}}{2\pi K_g l},$$

where Q is the heat loss (corrected for radiation) from a wire of length l, r_2 and r_3 the internal and external radii of the tube and K_g the thermal conductivity at an average temperature $\frac{T_2 + T_3}{2}$ of the glass used. Values of K_g at the appropriate temperatures were calculated in terms of the data obtained by Stephens,* who showed that the conductivity of Pyrex glass could be represented accurately by the relation

$$K_g{}^T = -0 \cdot 00352 + 0 \cdot 00245 \log_{10} T$$

over a range of temperature from $-182°$ to $250°$ C, where T is temperature on the absolute scale.

Radiation Correction

The correction to be applied for the emission of heat by radiation from a wire maintained at a certain temperature to a coaxial surface maintained at a lower temperature is not of very serious importance in the hot wire method, owing to the very small dimensions of the wires used. In the present series of experiments, the maximum correction was found to be of the order of 0·5% of the total heat transfer.

An exact determination is one of great difficulty. The experimental procedure as originally adopted by Gregory and Archer† was to evacuate the tubes as completely as possible and determine the heat loss under similar conditions of temperature as those imposed in the presence of a gas. It should be pointed out, however, that the temperature distribution along an electrically heated wire is not the same in the two cases and for this reason the present method of compensating end effects by using a long and short system of tubes and wires no longer holds. In addition, even in the best vacuum experimentally attainable, there is a heat transfer by conduction through a strongly rarefied gas which according to Knudsen is directly proportional to the gas pressure and comparable in magnitude with the radiation loss.

* 'Phil. Mag.,' vol. 14, p. 897 (1932).

† 'Proc. Roy. Soc.,' A, vol. 110, p. 91 (1926).

If Q denotes the total heat loss from a wire of length l and radius r_1 maintained at a temperature T_1 to a surrounding tube at a temperature T_2, then

$$Q = 2\pi r_1 l \varepsilon (T_1 - T_2)\, a P + \phi (T_1, T_2),$$

where ε represents the molecular conductivity, P the gas pressure and a the coefficient of accommodation, while $\phi (T_1, T_2)$ is the loss by radiation corresponding to the existing temperature conditions. If T_1 and T_2 are constant, then a linear relation holds between Q and P since a and ε are independent of pressure, from which $\phi (T_1, T_2)$ is known from the intercept on the Q axis. The procedure can be repeated for various values of T_1 and T_2 ($T_1 > T_2$) and ϕ determined for any chosen temperatures of the wire and wall and which represents a criterion of application in the present experiments.

Such an investigation was carried out by Milverton* with respect to the radiation from bright platinum and his results were expressed by a formula of the type

$$\phi (T_1, T_2) = 1\cdot 87\, (T_1^{3\cdot 82} - T_2^{3\cdot 82})\, 10^{-14} \text{ calories per cm of wire,}$$

in which T_1 and T_2 refer to the absolute temperatures of the wire and wall.

The above expression was employed to calculate the corrections applied to the results in the present paper.

The author has also calculated the radiation correction by using a formula deduced from theoretical considerations by Helfgott,† viz.,

$$E = \sigma T^4 (1 - e^{-\alpha T}),$$

where $\sigma = 5\cdot 72 \times 10^{-12}$ watts per cm² and α has the value $1\cdot 25 \times 10^{-4}$ for platinum, T denoting temperature on the absolute scale. The substitution of such data in place of the values calculated from Milverton's relation introduces a change in the thermal conductivity of the order of 1/15%, which is beyond the estimated accuracy of the present investigation.

Experimental Procedure

Apart from the important modifications referred to above, the arrangement of the experimental apparatus is similar to that employed by Gregory and Archer‡ in their experiments on the truth of Maxwell's

* 'Phil. Mag.,' vol. 17, p. 397 (1934).
† 'Z. Phys.,' vol. 49, p. 555 (1928).
‡ 'Phil. Mag.,' vol. 1, p. 593 (1926).

law of heat conduction. The procedure followed in a typical set of observations corresponding to a definite temperature of the wire is outlined below.

If the fundamental interval of the compensated platinum wire of length l has been determined, the bridge setting for any fixed wire temperature T_1 is known in terms of this along with the resistance at 0° C. If now the heating current in the thermostat is adjusted until a definite rate of cooling of the oil is operative, the current in the bridge circuit is adjusted by means of the rheostats in the battery circuit to a point where the balancing current through the tubes is slightly too high, as indicated by a definite deflection of the galvanometer. Such a deflection, if the balancing current is kept constant, will gradually be nullified in view of the increasing magnitude of $(T_1 - T_2)$ with time due to the cooling of the thermostat and eventually balance of the bridge circuit is effected. The temperature of the external wire is observed simultaneously with a measure of the balancing current, obtained with the potentiometer. The gas pressure is then decreased by a known amount and the procedure repeated. It is then found that in the absence of convection a definite change of balancing currents results, a change which is due to the increase of the temperature drop effect by reason of the decrease of gas pressure. The same holds for all other decreases in the gas pressure. It is found that the effect rapidly increases as the pressure is lowered by successive amounts and a point is ultimately attained where the time required for balance changes from an interval of about 5 minutes to a period of some hours; the current is found to require repeated adjustment in value to maintain constancy of the wire temperature. Since the cooling of the bath is in a direction such as to require the current to be increased, this effect must depend on some change occurring at the wire surface and is interpreted as being due alone to progressive changes in the film of gas adsorbed on the surface of the wire. The author has sought to express such changes in terms of the variation with time of the surface energy of the associated gas solid phase and this will be discussed in a subsequent paper from the aspect of the variation of the accommodation constant with pressure. In passing, it is emphasized that the method employed is such as to show conclusively that such effects are dependent alone on a change of surface conditions of the gas solid phase.

Typical sets of such observations are recorded in Tables II and III, and are expressed as a change of the balancing current with pressure.

The quantities $\frac{Q}{\theta}\log\frac{r_2 - \lambda'}{r_1 + \lambda}$ and $\frac{1}{P}$ can be calculated from such data and plotted to exhibit their dependence on each other in a linear relation.

TABLE II

Resistance of wire = 8·739 ohms; radiation = 0·00125 cal; (θ_p) temperature of wire = 328·91° C.

1/P	Current amps	θ_w° C	θ_g° C	$\frac{Q}{\theta}\log\frac{r_2-\lambda'}{r_1+\lambda}$
0·01257	0·3789	311·67	0·20	0·08678
0·01925	0·3771	311·72	0·20	0·08611
0·03008	0·3755	311·67	0·20	0·08505
0·04476	0·3733	311·61	0·20	0·08362
0·06477	0·3700	311·56	0·19	0·08163
0·09488	0·3649	311·52	0·19	0·07902
0·13812	0·3574	311·47	0·18	0·07521
0·19455	0·3475	311·42	0·17	0·07043

Mean temperature = 320·4° C.
Intercept = $2\pi Kl$ = 0·0875
K = 708 × 10^{-6} cal cm^{-1} sec^{-1} deg^{-1}.
Slope = 0·0868.
a = 0·236.

TABLE III

Resistance of wire = 6·107 ohms; radiation = 0·000355 cal; (θ_p) temperature of wire = 145·94° C.

1/P	Current amps	θ_w° C	θ_g° C	$\frac{Q}{\theta}\log\frac{r_2-\lambda'}{r_1+\lambda}$
0·01250	0·3573	132·42	0·14	0·07260
0·01595	0·3588	132·32	0·14	0·07298
0·02000	0·3593	132·22	0·14	0·07259
0·02487	0·3591	132·18	0·14	0·07227
0·03413	0·3582	132·15	0·14	0·07169
0·04464	0·3572	132·13	0·14	0·07112
0·05984	0·3558	132·10	0·14	0·07029
0·08842	0·3527	132·02	0·14	0·06854
0·18149	0·3412	132·00	0·13	0·06353

Mean temperature = 139·25° C.
Intercept = $2\pi Kl$ = 0·0736.
K = 595 × 10^{-6} cal cm^{-1} sec^{-1} deg^{-1}.
Slope = 0·055.
a = 0·239.

The values of λ' and λ corresponding to known wall and wire temperatures are calculated from the recent data of Trautz and Stauf* on the effect of temperature on the viscosity of hydrogen, the formula employed being

$$\lambda = \frac{2 \cdot 02\ \eta}{\sqrt{P\rho}},$$

where η is the viscosity of the gas at the appropriate temperature, P one atmosphere in dynes per cm^2 and ρ the density of the gas at N.T.P.

Apparatus and Results

The single compensated tube system used in the present series of experiments was made of Pyrex glass, and the principal constants of the apparatus were as follows:—

radius of platinum wire (r_1), 0·00397 cm;
length of principal wire, 24·81 cm;
length of compensating wire, 5·13 cm;
effective length of wire (l), 19·68 cm;

internal radius of tube (r_2), 0·757 cm;
external radius of tube (r_3), 0·992 cm;

resistance of internal wire at 0° C, 3·899 ohms;
resistance of internal wire at 99·64° C, 5·417 ohms;

fundamental interval, 1·518 ohms;

resistance of external wire at 0° C, 1·083 ohms;
resistance of external wire at 100·49° C, 1·498 ohms;

fundamental interval, 0·415 ohms.

In Tables II and III showing typical sets of observations the following symbols are used:—

P the pressure of the gas in cm of mercury;
θ_w° C, the temperature of the external wall of tubes;
θ_g° C, the temperature correction for the wall of the tubes;
θ° C, the temperature difference between the wire and the internal wall of the tubes;
Q, the total heat loss in calories from the wire, given by $C^2R_{\theta_r}/J$, corrected for radiation;
θ_p° C, the temperature of the wire.

$$\theta = \theta_p - (\theta_w + \theta_g).$$

* 'Ann. Physik,' vol. 2, p. 737 (1929).

The lines obtained for various wire and bath temperatures are shown in fig. 4 and indicate the accuracy of the observations.

The intercepts of such lines enable K to be found corresponding to a mean temperature between those of the wire and internal surface of the tube, the latter temperature being determined as explained above.

The slopes of the lines are the measures of the quantity from which the accommodation constant a is known. The linear form of equation (11) above for the range of pressures considered is a proof that a is independent of pressure over this range and depends only on temperature.

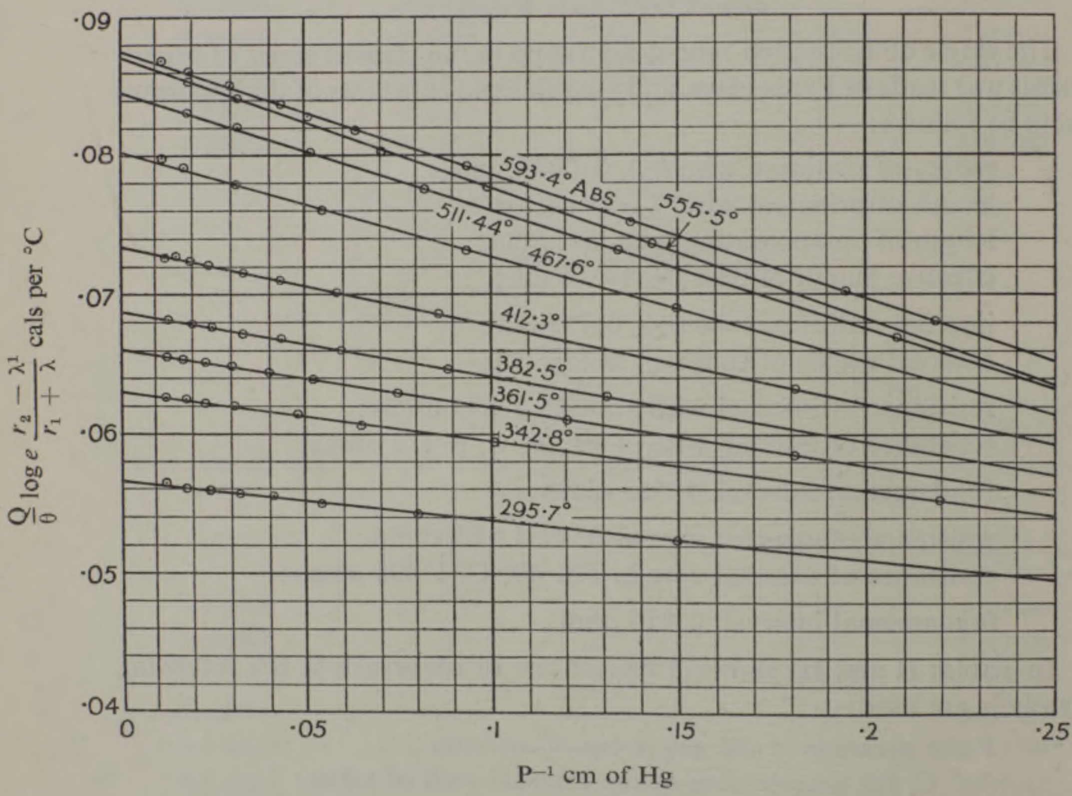

FIG. 4

The values of K referred to a mean gas temperature are tabulated in Table IV and are represented graphically in terms of such temperatures in fig. 5.

The graph in fig. 5 is marked by a definite change of dK/dT in the neighbourhood of about 230° C. Such a change might be reasonably interpreted as an effect due to gas impurities in the hydrogen associated with a lower thermal conductivity than in the pure state. The point

TABLE IV

Mean absolute temperature of gas T°	K × 10⁶	Absolute temperature of wire T_1°	*a*
593·4	708	601·9	0·236
555·5	704	564·2	0·213
511·4	689	520·2	0·211
467·6	651	475·5	0·216
412·3	595	418·9	0·239
382·5	558	389·4	0·252
361·5	534	368·0	0·259
342·8	512	349·4	0·269
295·1	459	299·4	0·282

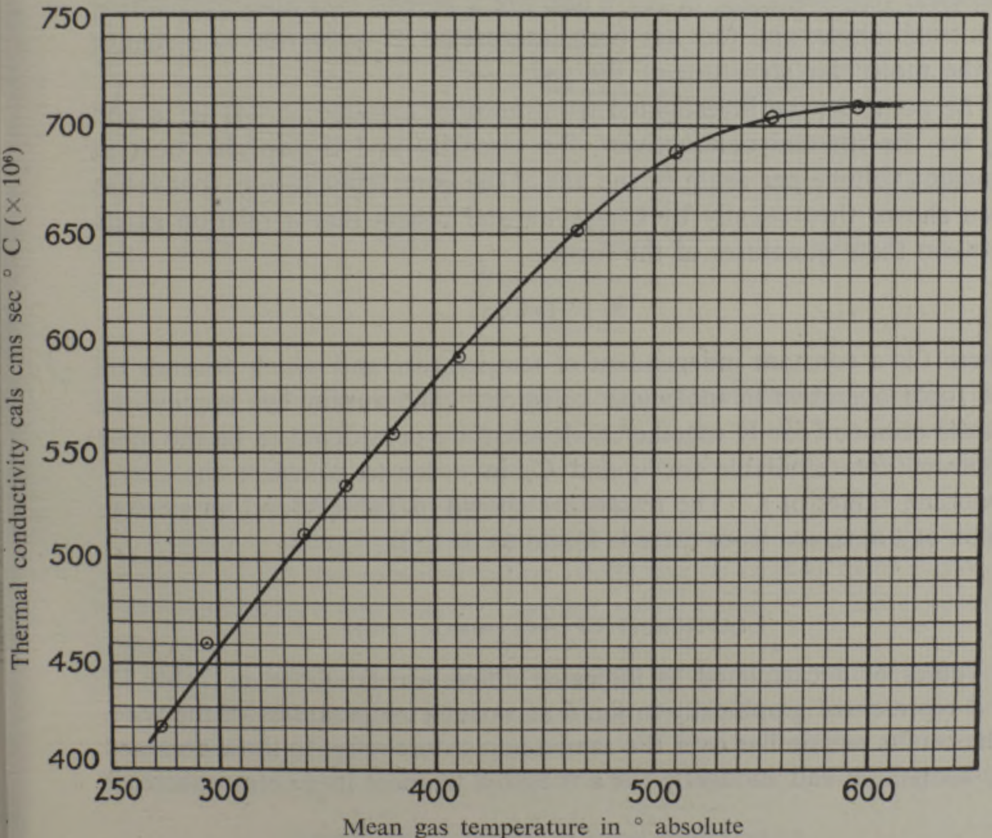

FIG. 5

was investigated by the author from the aspect of repeated observations, but no discrepancy of more than 0·5% was found amongst the determinations.

If the values of log K are plotted against the values of log T, where T is the absolute mean gas temperature, then for a range of about 230° a linear relation is found to hold. Beyond this range a linear law is still operative, but the line makes a smaller angle with the log T axis.

The equations expressing the above variations are found to be

$$K_T = 5 \cdot 68 \times 10^{-6} . T^{0 \cdot 77}$$

between 270° K and 502° K, and

$$K_T = 2 \cdot 2 \times 10^{-4} , T^{0 \cdot 19}$$

above 500° K.

In a paper on the effect of temperature on the viscosity of carbon dioxide Ibbs and Wakeman* discuss a similar effect. In this case the graphical representation of log η and log T reveals two lines intersecting at a small angle, and this has been interpreted as being due to a change in the molecular structure of the gas.

The point can be investigated from another standpoint. If K, η and C_v are the thermal conductivity, the viscosity and the specific heat at constant volume per gram of the gas at the same temperature, then it has been shown theoretically by Chapman and others that a relation exists between these quantities of the form

$$K = f\eta C_v,$$

where f is a constant independent of temperature and which depends on the force operative in molecular collision. The author has applied the results obtained for K together with what are considered to be the most accurate data available for η and C_v in order to calculate the corresponding values of f. The results are shown in Table V and an average value of f obtained from these is found to be 2·2.

Coefficient of Accommodation

Values of a calculated as indicated above are tabulated in Table IV and represented graphically in fig. 6 at various temperatures of the wire. The results are similar over the same temperature range to those obtained by Langmuir and Blodgett† for a tungsten filament in an atmosphere of

* 'Proc. Roy. Soc.,' A, vol. 134, p. 613 (1932).
† 'Phys. Rev.,' vol. 40, p. 78 (1932).

TABLE V

Absolute temperature of wire T_1	$K \times 10^6$	$\eta \times 10^7$	C_v	f
601·9	708	1437	2·50	1·97
564·2	705	1369	2·49	2·07
520·2	692	1290	2·47	2·18
475·5	658	1211	2·46	2·21
418·9	602	1109	2·44	2·23
389·4	567	1057	2·43	2·21
368·0	542	1019	2·42	2·20
349·4	519	986	2·41	2·18
299·4	464	896	2·40	2·16

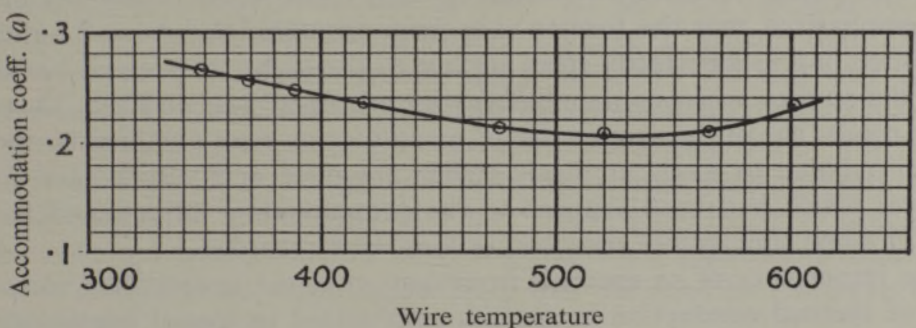

FIG. 6

hydrogen, and also by Mann* in a recent investigation. In the latter instance it was shown that the magnitude of the coefficient of accommodation depends to a great extent on the actual condition of the surface of the wire at the time of the experiment.

Roberts,† using tungsten filaments surrounded by strongly rarefied helium, found the accommodation coefficient to change from 0·057, the value found for a newly flashed surface, to 0·19 after 24 hours' exposure to the gas.

These results suggest that the increase in the value of *a* is associated with the formation of adsorption films by molecules drawn from the surrounding gas, the upper surface of which would consist of a loosely bound configuration of molecules for which *a* would be correspondingly

* 'Proc. Roy. Soc.,' A, vol. 146, p. 776 (1934).
† 'Proc. Roy. Soc.,' A, vol. 129, p. 146 (1930).

large. Such conclusions are in agreement with the investigations of Knudsen* in relation to roughened and blackened surfaces.

During the course of the present series of observations it was found that below a certain pressure, and this again depends on the temperature, the time required for attainment of the steady state changed from a period of several minutes to one of many hours. The current strength required to maintain constancy of the wire temperature was found to decrease rapidly at first and after some hours remained fixed in value. Such changes in the current at constant temperature and constant pressure point to progressive changes in the condition of the surface film with time. Although the agreement between various observers does not lead to any definite conclusion on the subject, yet the results at various pressures lower than those considered by the author suggest a variation of a with pressure at constant temperature.

In comparing the results of Mann (*loc. cit.*) with those of the author, it is emphasized that the former vary from an extrapolated small value corresponding to a perfectly clean surface to the higher values associated with the surface when contaminated with adsorbed gas, and that these latter results are of the same order of magnitude as were obtained by the author relative to gases at much higher pressures and with regard to surfaces which had been exposed to the contaminating influence of the gas for some time before the observations were recorded.

The importance of an accurate investigation of the temperature variation of thermal conduction in gases is emphasized in special relation to measurements of the coefficient of accommodation and the associated examination of the gas-solid phase.

The recent development of such measurements for hydrogen by Langmuir and Blodgett† may be considered from the point of view of comparison between their method and that used by the author. In their investigation of the accommodation coefficient for the hydrogen-solid phase, a modified hot wire method was employed.

Langmuir, in common with other investigators of the accommodation constant a, has regarded a state of rarefaction to exist adjacent to the wire, and a is defined as being the ratio of the experimentally observed heat loss Q_c to the calculated loss Q.

i.e.,
$$a = Q_c/Q, \tag{12}$$
where Q is known in terms of the temperature drop $T_1 - T'$, the molecular conductivity ε_k and the pressure P of the gas.

* 'K. danske vidensk. Selsk. Skr.,' vol. 9, p. 1 (1930).

† 'Phys. Rev.,' vol. 40, p. 78 (1932).

a can be calculated from (12) since T′ can be found from the relation

$$Q_c = \frac{2\pi l \int_{T_2}^{T'} K \, . \, dT}{\log_e \dfrac{r_2}{r_i + \lambda}},$$

where T_2 is the temperature of the tube wall and K is known as a function of the temperature from the equation

$$K = A \, . \, T^n,$$

A and n being constants.

In Langmuir's experiments use was made of Eucken's* data on the thermal conductivity of hydrogen between the temperature of liquid nitrogen and 100° C.

The excellence of the method lies in the fact that although the wire temperatures extended as high as 1600° K, the bath temperature being 92° K, in no case was the calculated value of T′ greater than 226° K, corresponding to a temperature drop of 1374°. In this way it was sufficient to make use of data on thermal conduction only over a limited range of temperatures and at temperatures lower than 0° C. The author has calculated T′ in Langmuir's experiments from data obtained at low temperatures in conjunction with Mr. Dock; the effect is to change the temperature drop from 1374° to 1356 ° and, when applied to a calculation of a, gives a value which differs from that obtained by Langmuir by an amount of only 1%.

In Langmuir's experiments the variation of K with temperature was of secondary importance only in the calculation of a, whereas in the author's experiments it is of primary importance.

Summary

The paper describes a modification of the hot wire method of investigating thermal conduction in gases in which the influence of convection and the temperature drop effect are eliminated in one operation. The method is applied to hydrogen over a range of temperature up to about 300° C.

An electrically heated oil thermostat was used as a constant temperature bath, the temperature of the tube wall being determined by means of a platinum wire fused on to the wall. Allowance was made experimentally for the gradual heating of the tube wall by regulating the heating current in the thermostat.

* 'Phys. Z.,' vol. 14, p. 324 (1913); vol. 12, p. 1101 (1911).

Corrections were applied for the loss of heat by radiation through the gas, and also for the temperature fall across the tube wall.

The values of the thermal conductivity of hydrogen, varying from 0·000459 cal cm^{-1} sec^{-1} deg^{-1} at 295·1° K to 0·000708 at 593·4° K, and of the accommodation coefficient for the hydrogen-platinum phase are given.

The variation of the thermal conductivity of hydrogen with temperature is expressed in the form

$$K_T = A \cdot T^n.$$

The accommodation coefficient is found to have a minimum value of 0·21 at 520° K and to be independent of pressure over the range of pressures considered.

Investigations on the Spectrum of Selenium V—Structure of Se II

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[Plates 2 and 3]

Introduction

Besides the very early work summarized in Kayser's 'Handbuch' the first considerable list of lines due to singly ionized selenium was given by L. and E. Bloch* in 1930. These authors used an electrodeless discharge through selenium vapour and ascribed the lines to the several stages of ionization of the atom by inserting a variable auxiliary gap in series with the discharge tube. Lacroute† also investigated the spectrum from λ 2200 to λ 1200. These measurements, however, were not sufficiently complete, and did not extend far enough into the extreme ultra-violet to enable an analysis of the spectrum of Se II to be undertaken, and up to the present there are no published records of any attempts at such an analysis.

* 'C. R. Acad. Sci. Paris,' vol. 185, p. 761 (1927) ; vol. 187, p. 562 (1928) ; 'Ann. Physique,' vol. 13, p. 233 (1930).

† 'J. Phys. Radium,' vol. 9, p. 180 (1928).