A NOTE ON THE HOT WIRE METHOD FOR MEASURING HEAT CAPACITY OF GASES AT LOW PRESSURES

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ABSTRACT

A hot wire cell has been devised for measuring the specific heat of gases at low preasures, in particular of vapours below their normal boiling point. The method is based on the heat loss from an electrically heated fine wire immersed in the fluid. When the pressures are greater than about 10 torr, the heat loss is proportional to the thermal conductivity of the gas, while at pressures below 1 torr, the heat loss depends on the specific heat. Thus, in a single experiment the thermal conductivity, the accommodation coefficient and the specific heat of the gas are determined. Measurements on dry air at 0°C and 40°C are reported.

1. INTRODUCTION

The hot wire cell method of evaluating the heat capacity of gases at constant volume has some advantages over the other methods. Firstly, only a small amount of gas sample is required and secondly it is possible to measure the heat capacity of gases at low pressures. The low pressure specific heat is the ideal value which can be directly compared with the spectroscopic calculations. Moreover it is possible to study the specific heat of vapours at a temparature below their normal boiling point. This feature is valuable because the region of interest in a few gases is at a temperature below their normal boiling point.

The hot wire assembly is widely used in other areas also. For example, it can be used to evaluate the thermal conductivity of gases[1] and has indeed been used for the measurement of thermal conductivity of vapours below their normal boiling point[2]. It is also used in aerodynamic studies to evaluate the velocity of flow of gases[3]. The present note is confined to a brief discussion of the specific heat measurements.

2. PRINCIPLE OF THE METHOD

The hot wire cell consists of an electrically heated wire of radius r_1, length L, mounted along the axis of a tube of radius r_2 The gas under investigation of molecular weight M is at a pressure p. A study of the heat transfer through gases[4,5] shows that when the mean free path λ of the gas is much smaller than r_1 the heat loss is proportional to the thermal conductivity of the gas. Molecular flow conditions occur near the wire when $\lambda >> r_1$ and over the whole tube if $\lambda >> r_2$. In the molecular flow region the heat loss from the wire at an absolute temparature T_2 to the tube at a temparature T_1 is given by

$$Q_g = 2\pi r_1 L p \alpha \left(\beta+\tfrac{1}{2}\right) \left[R/(2\pi M T_1)\right]^{1/2} (T_2 - T_1) \ldots \qquad [1]$$

In this expression, originally due to Knudsen[6], $\beta = C_v/R$ and α is the accommodation coefficient.

It is evident from Eqn. [1] that by studying the heat conductivity of the gas at low pressures it is possible to evaluate C_v, provided α can be obtained. Now the mechanics of gas interaction on the solid surface are quite complicated[4], and it is best to consider the a.c. as an effective parameter to be determined under the operating conditions. Therefore attempts have been made to evaluate α as well as C_v from the same arrangement.

Following the earlier suggestion of Eucken[7], Kistiakowsky and coworkers[8], assumed that the ratio of the α's for different gases approach unity at low temparatures and studied the specific heats of ethane etc, in relation to a standard gas, *viz.*, Argon. A different procedure was used by Vanderkooi and de Vries[9] following the earlier arrangement of Eucken and Krome[10]. A wire and a flat ribbon are both used inside the same outer tube. The heat losses determined in the usual way will be of the form

$$Q_{\text{wire}} = A_w (T_2 - T_1) p (M T_2)^{-1/2} + A_{wr} (T_2 - T_1) p (M T_2)^{-1/2} \qquad [2]$$

where A_w depends in addition to the geometrical parameters, on the a.c. α_{wire} and $(\beta + \frac{1}{2})$. A_{wr} is a coupling term depending on α_w and α_R. A similar equation holds for the ribbon also. α_w and C_v are obtained by studying the heat loss from the wire at different settings. A third procedure has been suggested by Gregory and coworkers[11]. They have used Eqn. [1] at low pressures. At high pressures the heat loss, including the temperature jump, is written as

$$\frac{1}{Q} = \frac{\ln(r_2/r_1)}{2\pi K L (T_2 - T_1)} + \frac{A}{p (T_2 - T_1)} \left[\frac{\sqrt{T_2}}{r_1} + \frac{\sqrt{T_1}}{r_2}\right]$$

where
$$A = \left(\frac{2\pi M}{R}\right)^{1/2} \frac{1}{2\pi L} \frac{2-\alpha}{2\alpha \left(\beta + \frac{1}{2}\right)} \qquad [3]$$

It is suggested that at 'high' preasures the plot of $1/Q$ against $1/p$ is a straight line from which K and $[(2-\alpha)/\alpha(\beta+\frac{1}{2})]$ can be known. This combined with the value of $\alpha(\beta+\frac{1}{2})$ obtained in the 'low' pressure Eqn, [1] enable all the quantities to be evaluated.

3 EXPERIMENTAL ARRANGEMENT AND RESULTS

Because of the interest in the study of the specific heat of some vapours below their normal boiling point, it seemed worthwhile to investigate the possibility of using a hot wire cell for the evaluation of the specific heats. Of the procedures for estimating α the method suggested by Gregory was adopted. It allows a simpler hot wire cell than the wire and ribbon procedure. Further, the thermal conductivity may also be compared with the standard values to check the procedure, whereas, such a check on *K* is not possible in the more complicated wire-ribbon method of Eucken. The method used by Kistiakowsky and coworkers does not appear to be free from objections.

Two compensated hot wire cells of the type used by Gregory and coworkers[11], have been used in the present arrangement; one cell was of glass and the other of copper. Platinum wire of radius 0.00375 cm has been used for the central wire. The glass cell had a diameter of 0.830 cm and the copper tube 0 625 cm. The compensating cell had a length of ~ 5 cms which is adequate for the elimination of end conduction. The glass cell had an effective length of *15.72 cms* and the copper *cell 13.90 cms. The hot* wires of the cell were included in the two arms of a Callendar Griffith Bridge. The temperature of the wire was measured by previously calibrating the platinum wire resistance as a functian of temperature. The current through the wire was measured by connecting a series standard resistance and using a Vernier potentiometer. The cells were placed in an ice bath or in an electronically regulated paraffin oil bath.

An all glass high vaccum apparatus was used for the purpose, A Toepler pump was used for adjusting the pressures while a manometer and a McLeod gauge were used to measure the absolute pressures. The vacuum techiques were of conventional design.

The observed heat loss I^2R should be corrected for several factors. The radiation loss is obtained by measuring the heat loss in the highest vaccum $\sim 10^{-6}$ torr. Convection effects under the conditions of the experiment are negligible if the hot wire cell is mounted vertically. Finally, the end losses are eliminated by employing, as mentioned above, a compensated pair of cells.

The two hot wire cells were tested with pure dry air at the two temperatures of 0° and 40°C. Figure (1) shows performance of the glass cell at $t_2 = 0°C$ and Figure (2) that of the copper cell at $\sim 40°C$. The plots are quite linear and the values of the various quantities obtained from the figures are :

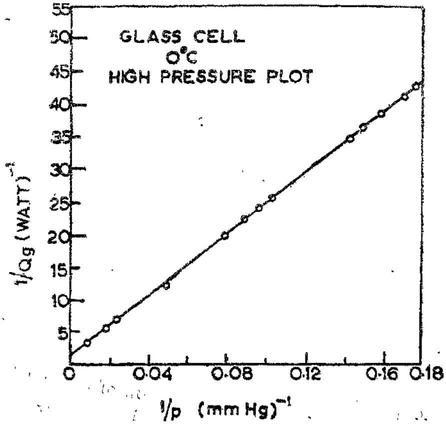

FIG. 1a

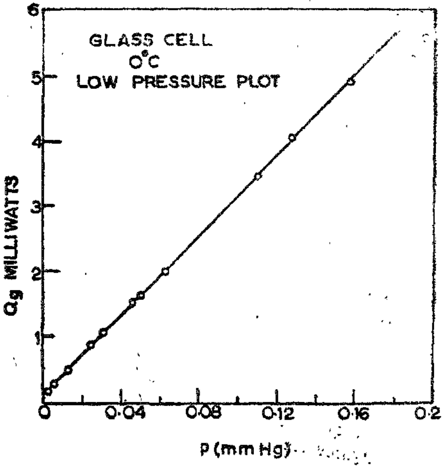

FIG. 1b

Behaviour of the glass cell at an ambient temperature of 40°C
(*a*) high pressure region. (*b*) low pressure region.

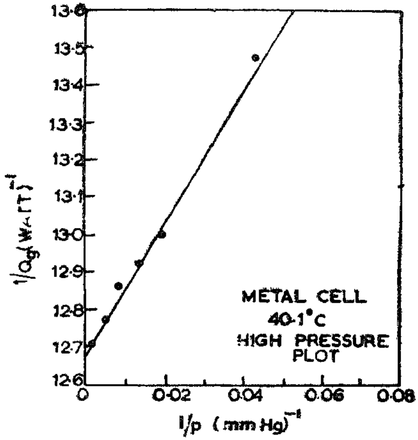

FIG. II a

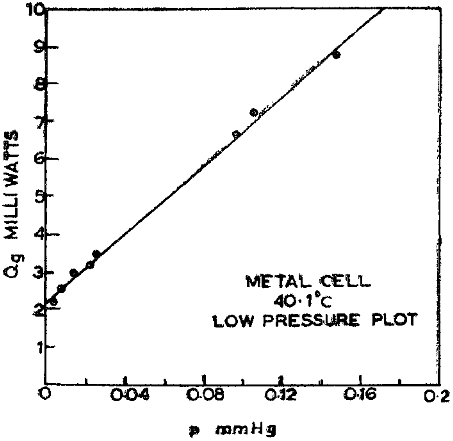

FIG. II b

Behaviour of the metal cell at an ambient temperature of 40°C.
(*a*) high pressure region (*b*) low pressure region.

At 0°C: $K = 5.8_1 \times 10^{-5}$ cal/cm deg. sec; $C_v/R = 2\ 5_0$; $\alpha = 0.48_4$

At 40°C: $K = 6.2_9 \times 10^{-5}$ cal/cm deg. sec; $C_v/R = 2.4_9$; $\alpha = 0.55_8$

The value of the specific heat is as expected very close to that of an ideal diatomic gas $C_v = (5/2)R$. The values of K compare well with the values, summarized for example, by Dickins[12]; K at $0°C = 5.84 \times 10^{-5}$ can/cm sec. deg. and K at $40°C = 6.5_1 \times 10^{-5}$. The value of the a.c. are not comparable for they refer to the specific experimental conditions. They are of the same order as those for fully absorbed surfaces. It is only for very clean surfaces in much higher temperatures that smaller values of α are obtained.

In conclusion, Gregory's method of evaluating the a.c. appears to be suited for using the hot wire cell to evaluate the specific heat vapours and that the present arrangement is suitable for studying gases under various conditions.

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