

temperature level. This procedure corrects for thermal expansion and its effect on the gas layer thickness and on the cell dimensions. Radiation between the surfaces which confine the gas layer changes only with the temperature difference across this layer and with the temperature level, provided the emissivities of the two surfaces do not change. This effect is taken into account in the calibration by using constant temperature difference at several fixed bath-temperatures. The heat is supplied by a platinum wire serving a dual purpose as a resistance thermometer. A wire has been used in this fashion by Michels and Botzen (1952). The other temperature is measured by a second resistance thermometer. The external bath-temperature is constant and is thermostatically controlled. The cell constants are determined by measuring the power input to the inner wire as a function of the thermal conductivity at atmospheric pressure at each bath temperature-level once with cylinder C in place and again with cylinder C' in place.

The condition which leads to convection has been shown by Nusselt (1929) to be adequately determined by the product $N_{Gr} N_{Fr}$ of the Grashof and Prandtl groups. Kraushold (1934) finds that a value of this product less than 600 gives good assurance that convection will not be present. This has been confirmed in a few cases at elevated pressures by Lenoir (1951) and also provides the basis for calculations confirmed by experiments indicating that convection is likely to occur in the vicinity of the critical, despite all efforts to avoid it (Leng and Comings 1957, Uhlir 1952).

DERIVATION OF CALIBRATION EQUATION

The heat transfer in the cell may be followed by reference to Fig. 5.5. The heat Q is generated in the coil wound on cylinder A. This flows radially through the resistance $\phi(k)$ which includes a thin gas film surrounding A and the resistance of cylinder B. There is also an end loss from B and the resistance for this heat flux is $g(T)$. The rest of Q flows radially through the gas layer conduction resistance E/k in parallel with the radiation resistance $f(T)$ and thence through the resistance ψ or ψ' of the cylinder C or C' and out through the bomb walls to the bath. If the temperature difference between the two platinum resistance thermometers is ΔT , then $\Delta T/Q_1$ is a complex function of k , $T_{ave.}$, and ΔT . This is evident from considering the several resistances at a given temperature level. $\phi(k)$ is constant except for changes in the thermal conductivity of the gas film. For a single gas in the cell this value will change with pressure. E_1 is a geometrical factor for the cell with C in place and E_2 is a similar factor with C' in place. These may change slightly owing to thermal expansion but each will have a single value at any one temperature. $g(T)$ varies slightly as the temperature of the end insulators changes but should be constant at a given temperature level. $f(T)$ depends on the difference in fourth powers of the temperatures on both sides of the gas layer, but it may conveniently be considered a function of $T_{ave.}$ and ΔT . ψ and ψ' are

essentially equal and change slightly with temperature. With ΔT and T_0 held constant either

$$\frac{1}{k} = k_1 (\Delta T/Q_1) \text{ at constant } T_0 \text{ and } \Delta T \quad (5.1)$$

or

$$\frac{1}{k} = k_2 \left\{ \Delta T \left(\frac{1}{Q_2} - \frac{1}{Q_1} \right) \right\} \text{ at constant } T_0 \text{ and } \Delta T \quad (5.2)$$

where k is the thermal conductivity of the gas, ΔT the temperature difference between the two platinum resistance thermometers, Q_1 the electrical energy input with C in place, Q_2 the electrical energy input with C' in place, and T_0 the external bath temperature.

CALIBRATION AND OPERATION

The cell is calibrated at atmospheric pressure for each value of the bath temperature by using several gases of known thermal conductivity. The measurements are repeated first with outer cylinder C in place and then with outer cylinder C' in place. Bath temperature, T_0 , temperature difference ΔT , between the two platinum coils, and the calibrating gas are all the same for these pairs of repeated measurements. The power Q supplied to the cell is different. The calibration establishes the relationship given in equation (5.2) for predetermined values of ΔT and T_0 .

This relationship is independent of pressure and is used to determine the unknown thermal conductivity of gases at elevated pressure. The procedure for making such determinations is as follows. The cell with outer cylinder C is sealed in the pressure vessel and a gas is introduced into the pressure vessel cavity and brought to a given pressure. The bath temperature and the ΔT across the platinum wires are adjusted to predetermined values. This requires the adjustment of Q_1 . The gas pressure is changed and Q_1 is again determined. In this way, Q_1 is obtained as a function of pressure for this gas at constant values of T_0 and ΔT . The cell is now dismantled and outer cylinder C is replaced by outer cylinder C'. The relation between Q_2 and pressure is now determined for the same values of T_0 and ΔT as were used for Q_1 . The quantity $\Delta T(1/Q_2 - 1/Q_1)$ is now evaluated at several pressures and the values of k corresponding to these pressures are read from the calibration curve. This procedure is then repeated at another bath temperature.

In a second method only one of the cylinders C or C' is used, thus avoiding difficulties in reassembling the cell exactly as it was calibrated. In this case, only the one value of Q is observed for each combination of conditions at constant T_0 and ΔT . By using several gases of known thermal conductivity a relation is established as

$$1/k = k_1 (\Delta T/Q_1) \text{ at constant } T_0 \text{ and } \Delta T \quad (5.1)$$

This is used to measure an unknown k by observing the value of Q for the same conditions of ΔT and T_0 as the original curve.

The experimental determinations of the thermal conductivity of gases at pressures above 5 atm. carried out