A Cylindrical Thermal Conductivity Cell for Gases at Pressures to 3,000 Atmospheres[†]

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INTRODUCTION

MEASURED VALUES of the thermal conductivity of gases at elevated pressures are needed in equipment and process design and they are of interest in connexion with the development of the theory of intermolecular action and transport. Recent measurements have shown wide deviations from predicted behaviour especially in the critical region (Leng and Comings 1957, Lenoir and others 1953)‡ and with gas mixtures (Junk and Comings 1953). The behaviour becomes more complex as the molecular structure becomes more complex. The critical region for mixtures extends to much higher pressures (Comings 1956) than for pure compounds.

APPARATUS

A thermal conductivity cell of relatively simple design has been constructed to operate at pressures up to 3,000 atm. and at temperatures up to about 400 deg. F. The thermal conductivity cell is contained in the cavity of a highpressure vessel constructed of SAE 4340 steel. The cavity is large enough to hold the cell with a clearance of about 3 inch thick annulus. The vessel closure is fitted with six electrical leads and with a connexion for admitting the gas under test to the cavity. An additional electrical lead passes through the body. The high-pressure vessel is completely immersed in a constant-temperature oil bath.

A diagram of the cell is shown in Fig. 5.5. Heat flows outward radially from a central copper cylinder B, across a thin layer of the test gas and into a copper cylinder C or C^I. Two interchangeable outer cylinders are used to provide two thicknesses of gas layers, about 0.006 and 0.009 inch respectively. B and S gauge 32 platinum wire, 0.00795 inch diameter, is wound in spiral grooves in the solid cylinder A. A high-temperature cement surrounds

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- 1 An alphabetical list of references is given in Appendix 5.II.



mica. Rings of moulding com-K E pound.

the wire and fills the grooves. Cylinder A is inserted through a hole in cylinder B. The platinum wire serves as both a heating element and a resistance thermometer. B and S gauge 38 platinum wires 0.0040 inch in diameter are wound in spiral grooves around the outside of cylinders C and C¹ in the same manner as for cylinder A. These wires serve as resistance thermometers. Heat flows from the cylinders C or C^I to the body of the pressure vessel through corrugated aluminium sheet (1/32 inch) arranged as shown in Fig. 5.6.

Steel bolts.

Axial heat flow from the inner cylinder B is reduced to a negligible proportion of that from the heating wire



Fig. 5.6. Final Assembly

by the solid disks D of '400' Supra-mica, a glass-bonded mica material. Axial heat flow in the outer cylinders C or C¹ is not a problem but moulding compound rings E of Dow Corning 301 moulding compound, a lowconductivity substance, are used.

The two gas layer thicknesses are determined for each outer cylinder C or Cⁱ by the three set screws J on each end. Each piece is marked to ensure reassembly in exactly the same position.

Other Designs

Cells for measuring the thermal conductivity of gases at high pressures have followed three designs with several modifications of each. These are the hot-wire design based on the early Schleiermacher (1889) design, the horizontal flat-plates design and the concentric-cylinders design.

In the hot-wire design the heat from an electrical resistance wire flows radially through a surrounding layer of gas. This design was used by Vargaftik (1937) and by Stolyarov, Ipatiev and Teodorovitch (1950). The thermal conductivity is determined by observing the temperature difference across the gas layer, the rate of heat generation in the wire and the thickness of the gas layer. Corrections must be made for heat conducted out along the ends of the wire. A serious problem arises when this design is used at high pressures. The clearance between the wire and the wall of the surrounding tube must be made so small to avoid convection, that it is almost impossible to centre the wire properly and measure the thickness of the gas layer with the required precision.

The horizontal flat-plate type consists of two flat plates with the gas in the space between them. The thickness of the gas layer is carefully determined by spacers. The upper plate is the hotter and heat flows downward so that the more dense gas is on the bottom as a precaution against convection. Heat flow at the edges of the gas space must be taken into account. This is done in the cell described by Michels and Botzen (1952) by using three different thicknesses of spacers and calculating the cell constants. The three measurements also permit an allowance to be made for heat transfer between the plates by direct radiation. Borovik (1947) used a horizontal platetype cell. Uhlir (1952) points out that Borovik found evidence of convection in his cell despite the desirable arrangement with the heat flowing downward. This arrangement alone does not ensure that convection will not be present and reliance must be placed on a layer which is sufficiently thin. In a cell of this type at the U.S. Bureau of Standards capacitance measurements were made to determine the cell constants by analogy between the heat flow and electric system.

Several variations of employing concentric cylinders have been used. Keyes (1951), Keyes and Sandell (1949) employed an electrically heated vertical inner cylinder and the heat flows out radially through a gas layer about 0.025 inch thick. Temperatures are measured on both sides of the gap and the electrical input, corrected for end losses, permits direct calculation of the thermal conductivity. This layer was thick enough to permit separation of the two components of a mixture by thermal diffusion (1954). Uhlir (1952) used a vertical cylinder with a gas layer thickness of 0.010 inch and a helium gas thermometer on both sides of the layer. Electric current was switched from an external heater to a heater in the cylinder during a measurement and the power, temperature difference, and cell dimension are used to calculate the thermal conductivity of argon. In the cell described by Lenoir and Comings (1951), horizontal concentric cylinders are used. The gas layer thickness is 0.006 inch and is thin enough to preclude convection in most circumstances. Heat flows inward radially from circulating water or oil (Leng 1957) in the jacket and is removed by circulating water or oil in a central tube. A second layer 0.030 inch thick containing a standard gas is used outside the test gas layer and no heat measurements are required. The cell is calibrated at atmospheric pressure with several gases of known thermal conductivity and temperatures only at three positions need be measured to calculate the thermal conductivity. This design is cumbersome and is probably not suited for measurements above a few hundred atmospheres since the walls of the gas layer are pressure-retaining walls and the gas layer is subject to distortion.

FEATURES OF CELL DESIGN

The elements of cell design and operation which are important when operating at pressures up to a few thousand atmospheres and temperatures to 400 deg. F. with gas mixtures in regions including the critical region are:

- (1) cell geometry including symmetry, and end effects;
- (2) gas layer thickness and position with respect to
 - avoiding convection and thermal diffusion effects;
- (3) pressure distortion effects;
- (4) thermal expansion effects;
- (5) radiation effects;
- (6) the heating and temperature measuring system;
- (7) the method of determining the cell constants whether by direct measurement, by calibration, or by analogue measurements.

The horizontal cylindrical type offers a symmetrical arrangement and provision can readily be made to minimize end effects or to correct for them. Very thin layers of gas combined with small temperature gradients offer the least possibility of convection and with these in a horizontal position no difficulty should be encountered from thermal diffusion. No appreciable error results from small eccentricity. Pressure distortion is eliminated if the cell is contained in the cavity of a pressure vessel and is immersed in the gas being tested. This arrangement requires a large gas sample and is thus not suited to measurements on rare or expensive gases. The cell constants are determined by calibration at atmospheric pressure against gases of known thermal conductivity at each

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^I in place.

The condition which leads to convection has been shown by Nusselt (1929) to be adequately determined by the product \mathcal{N}_{Gr} \mathcal{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^I and out through the bomb walls to the bath. If the temperature difference between the two platinum resistance thermometers is $\triangle T$, then $\triangle T/Q_1$ is a complex function of k, $T_{ave.}$, and $\triangle T$. 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 $T_{\text{ave.}}$ and $\triangle T$. ψ and ψ' are essentially equal and change slightly with temperature. With $\triangle T$ and T_0 held constant either

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

or

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

where k is the thermal conductivity of the gas, $\triangle T$ 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^I. 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 C¹ 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 $\triangle T$. By using several gases of known thermal conductivity a relation is established as

 $1/k = k_1 (\Delta T/Q_1)$ at constant T_0 and ΔT (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 up to this time are listed in Table 5.2. The measurements by Stolyarov, Ipatiev, and Teodorovitch were made in a cell of the hot-wire type with a wire inside a glass tube 0.6 mm. wide. The measurements reported by these authors are given in Table 5.3. The data in this table have been interpolated to provide values at definite temperatures and pressures.

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Table 5.2.	Thermal	Conductivity	Measurements	of	Gases
		above 5 ati	n.		

Gas	Pressure range, atm.	Temperature range	Refer- ence	
Air	1, 200, 400	11 to 188 deg. C.	19	
Ammonia	0 to 9.0	50 to 250 deg. C.	7	
Argon	1 to 100 1 to 217-4 1 to 194-1 0 to 19-5 1 to 2500	 87 to 194 deg. K. 127 deg. F. 106 deg. F. 90 to 350 deg. C. 0 to 75 deg. C. 	20 12 11 7 15, 16	
Benzene		0 to 346 deg. C.	- 1	
Carbon dioxide	1 to 205·3 1 to 300 1 to 60.6	106, 134, and 153 deg. F. 7 to 202 deg. C. 1 to 50 deg. C.	11 19 6	
Ethane	1 to 261 1 to 196 0 to 39·4	154 deg. F. 108, 134, and 153 deg. F. 52 deg. C.	10 - 12 7	
Ethylene	1 to 226 0 to 15·5	106 and 153 deg. F. 72, 153 deg. C.	11 7	
Ethylene and car- bon dioxide (2 mixtures)	1 to 199•9	108 deg. F.	4	
Ethylene and nitrogen (4 mixtures)	1 to 206.5	108 deg. F.	4	
Helium	1 to 205·2	. 109 deg. F.	11	
Hydrogen 1 to 206-7 1 to 500 0 to 144-8		109 deg. F. 14 to 302 deg. C. 85 to 250 deg. C.	11 19 7	
<i>m</i> -Xylene		0 to 346 deg. C.	1	
Methane	1 to 203.4 1 to 500 1 to 203 0 to 60.5	106 deg. F. 11 to 212 deg. C. 127 deg. F. 50 to 300 deg. C.	11 19 12 7	

Gas	Pressure range, atm.	Temperature range	Refer- ence		
Nitrogen	11.2 to 99 1 to 2500 1 to 216.7 1 to 150 1 to 90 1 to 205.7 5.8 to 67 1 to 143.4 1 to 500	 -183 to -103 deg. C. 25, 50, 75 deg. C. 127 deg. F. to 400 deg. C. 40 to 62 deg. C. 106 deg. F. 76 to 184 deg. C. 0 to 50 deg. C. 12 to 298 deg. C. 	2 13 12 8 21 11 20 6 19		
Nitrogen and car- bon dioxide (3 mixtures)	1 to 84·3	0.6 to 50 deg. C.	6		
Nitrous oxide	0 to 52.7	50 deg. C.	7		
Oxygen	1 to 96.8	-117.0 deg. C.	2		
Propane	1 to 282	122 to 284 deg. F.	10		
Steam	5 to 28 to 150	250 to 355 deg. C. 250 to 500 deg. C.	21 5, 8		
Toluene		0 to 346 deg. C.	1		

Table 5.3. Thermal Conductivity Measured by Stolyarov, Ipatiev and Teodorovitch 1950

 $k = 10^7 \times \text{cal per cm. sec. degree C.}$ Pressure kg per sq. cm.

	t, deg. C.	• 1	100	200	300	400	
Hydrogen	15	4190	4309	4463	4561	4591	
	100	5050	5110	5215	5268	5303	
	200	6025	6064	6142	6183	6212	
	300	7000	7029	7095	7134	7146	
Nitrogen	15	600	674	871	1038	1128	1
	100	735	761	907	1049	1124	1
	200	888	898	983	1088	1151	l
	300	1030	1035	1097	1182	1233	ł
Air	20	615	665	910	1082	1207	-
	100	730	737	897	1030	1121	ł
	180	865	872	975	1833	1160	
Methane	20	800	1080	1565	1808	1956	Ì
	100	1085	1173	1479	1668	1784	ł
	200	1420	1448	1675	1750	1840	i
Carbon	53	460	1336	2006		_	1
dioxide	85	520		1548	1902	_	ļ
	100	560	812	1461	1836		Ì.
	150	665	735	1169	1529	_	1
	200	765	790	1069	1383	-	

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APPENDIX 5.II

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