

A New Method for Measuring the Atomic Heats of Gases

In a previous communication in *Nature*¹, a method was described by which the atomic heats of various gases could be determined from the aspects of heat transfer through the gas. The method has recently been modified to take into account the dependence of the accommodation coefficient upon the pressure of the gas at very low pressures.

In the absence of convection, the rate of heat loss Q corrected for radiation from a uniformly heated thin platinum wire lying along the axis of a cylindrical tube can be represented in terms of the gas pressure P by an equation due to Knudsen and others in the form:

$$Q = 2\pi r_1 L P (R/2\pi M T_2)^{1/2} (\beta + \frac{1}{2}) \alpha_P (T_1 - T_2), \quad (1)$$

in which the mean collision path is greater than, or comparable with, the distance between the wire and the internal surface of the tube. In (1), βR represents the molecular heat of the gas, α_P the coefficient of accommodation, T_1 and T_2 the temperatures of the wire and tube surfaces respectively, r_1 the radius and L the length of the wire, and M the molecular weight of the gas.

Values of α_P calculated from (1) at very low pressures are found to vary considerably with the pressure up to the region in which the temperature-drop effect operates and throughout which the values of α_P are independent of the gas pressure. In this latter range of pressures the modified Fourier's relation is represented² by:

$$\frac{1}{Q} = \frac{\log(r_2/r_1)}{2\pi r_1 K L \theta} + \frac{1}{P \theta A} \left(\frac{T_1^{1/2}}{r_1} + \frac{T_2^{1/2}}{r_2} \right), \quad (2)$$

where the term A is defined by:

$$A = \frac{R^{1/2} 2\pi (\beta + \frac{1}{2}) 2\alpha L}{(2\pi M)^{1/2} (2 - \alpha)}$$

If the temperature of the wire is kept constant over both ranges of pressures, and if α_P is known as a function of pressure and temperature, β can be calculated. Equation (1) must be modified, using the Langmuir adsorption equation:

$$\theta/N_0 = bP/(1 + bP),$$

where θ denotes the number of lattice spaces per square centimetre of the wire surface which are occupied by gas molecules at a pressure P and temperature T , and N_0 denotes the total number of lattice spaces per square centimetre. The effect of accommodation may be considered as being due to the extent to which the lattice spaces are occupied by molecules. Hence we may write for α_P , following Amdur³,

$$\alpha_P/\alpha_\infty = \theta/N_0 = bP/(1 + bP), \quad (3)$$

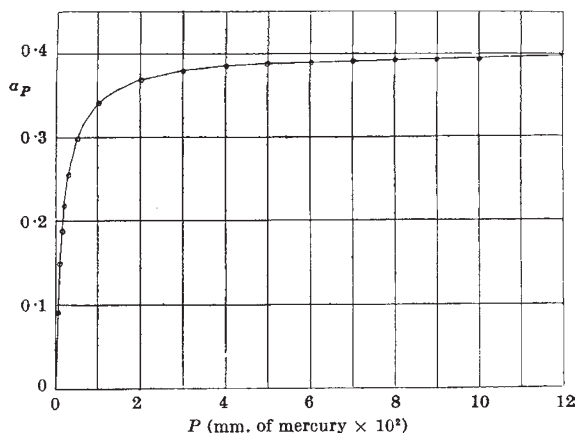
where b is a function of temperature and α_∞ denotes the coefficient of accommodation over the temperature-drop range of pressure.

Equation (1) may now be written in the form:

$$\frac{P^2}{Q} = \frac{1}{2\pi r_1 L (R/2\pi M T_2)^{1/2} (\beta + \frac{1}{2}) \alpha_\infty (T_1 - T_2)} \left(\frac{1}{b} + P \right),$$

from which P^2/Q is found to satisfy a linear relation with P . At the same time, $1/Q$ has been found to satisfy a linear relation with $1/P$ over the temperature-drop range of pressure at the same wire temperature as in (1).

It is therefore possible to determine β and α_∞ and also a value of b . The accompanying graph shows



the variation of α_P with P as quoted from equation (3) by the substitution of α_∞ and b for hydrogen at a wire temperature of 19°C. From the graph it appears that α_P rises very sharply with P at very low pressures. The table shows observed values of α_∞ and β for a number of gases at laboratory temperatures.

Gas	H ₂	N ₂	O ₂	He	Ne	A
β	2.49	2.50	2.49	1.49	1.49	1.50
α_∞	0.40	0.81	0.80	0.42	0.78	0.84

The method has also recently been applied in order to investigate the decrease of the rotational energy of hydrogen, oxygen and nitrogen at very low temperatures.

It is hoped to publish a detailed account later.

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¹ Gregory and Stephens, *Nature*, **139**, 28 (1937).

² Gregory, *Phil. Mag.*, (7), **22**, 257 (1936).

³ Amdur, *J. Chem. Phys.*, **14**, 339 (1946).

Quantitative Paper Chromatography

Fisher, Parsons and Morrison¹, discussing quantitative paper chromatography, found an interesting relationship between spot-length or spot-area and the logarithm of spot content for certain amino-acids and the sugars xylose and arabinose. They suggest that the relationship may be of general applicability to sugars.

Using Longenecker's method² for ascending chromatography (somewhat modified), with 500-ml. and 1-litre jars and papers 5 mm. wide, measuring spot-length instead of spot-area, an attempt has been made to confirm this work using saturated *n*-butanol-water mixture (water-poor phase) as solvent and sucrose as the sugar. Spraying was carried out with the phloroglucinol reagent mentioned by Horrocks in his paper³. Spot-length instead of spot-area was chosen for measurement because maximum elongation can fairly easily be measured with practice on narrow papers, and the work was intended for rapid assessment of quantitative differences. Sucrose was chosen in preference to xylose or arabinose for investigation, because it is of more interest in studying the nutritional requirements of plants and gives a clear