Physical Chemistry

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1964

SovietRxiv

Abstract

Full Text

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THEORY OF THE THERMOMOLECULAR PRESSURE DIFFERENCE AND THERMOTRANSPIRATION (THERMOOSMOSIS) OF GASES IN MODERATELY WIDE CAPILLARIES

In a paper by one of us (1), a theory was developed for the thermomolecular pressure difference of gases in wide capillaries in the limiting case

$$\mathrm{Kn} \equiv \frac{\lambda}{R} \to 0, \tag{1}$$

where Kn is the Knudsen number, R is the radius of the capillary, and λ is the mean free path of gas molecules. This theory, in contrast to Maxwell' s theory, is based on the third approximation of the Chapman–Enskog kinetic theory of gases (2), which makes it possible to consider phenomena in the volume of a nonuniformly heated gas. It was shown that the formula derived agrees satisfactorily with Knudsen' s measurements (3) (at pressures above 13 mm Hg), which exceed the values calculated from the formula derived by Maxwell (4) by more than a factor of two. In the present work, the result of (1) is refined by taking into account first-order effects in Kn, which makes it possible to extend the range of applicability of the theory to moderately wide capillaries.

Similarly, in (5) the theory of thermophoresis of large aerosol particles (6), also developed on the basis of the Chapman–Enskog theory (2), was refined by taking into account first-order terms in Kn, as a result of which a formula was obtained that is applicable to particles with intermediate and large values of Kn.

In a number of works (7-13), Maxwell' s formula for the thermomolecular pressure difference in wide capillaries was generalized with the aim of bringing it into agreement with experimental data. However, agreement with experiment is achieved only for such values of the constants as contradict Maxwell' s calculations and, by turning the formula into a purely empirical one, make it impossible to speak of its experimental confirmation.

It was shown that an analogous refinement (14,15) of the theory of thermophoresis in gases (16), constructed on the basis of Maxwell' s thermal-slip formula, is incapable of bringing it into agreement with experiment (^{17}). Thus, verification and refinement of the theory of the thermomolecular effect and of thermal transpiration are directly relevant also to the theory of thermophoresis of aerosol particles.

Let us consider, as in (^{1}), a system consisting of two vessels with gas, connected by a capillary of radius R and length a. Suppose that constant temperatures T_1 and T_2 and pressures p_1 and p_2 are maintained in the vessels. Then at the ends of the tube there will be a temperature difference:

$$\Delta T = T_1 - T_2$$

and a pressure difference

$$\Delta p = p_1 - p_2.$$

In this case, fluxes of matter and heat will arise in the capillary (^{18})

$$I_M = -\alpha_{11}\frac{\Delta p}{\rho T} - \alpha_{12}\frac{\Delta T}{T^2},$$

$$I_Q = -\alpha_{21}\frac{\Delta p}{\rho T} - \alpha_{22}\frac{\Delta T}{T^2}. \tag{2}$$

We are interested in the stationary state under the condition

$$I_M = 0, \tag{3}$$

corresponding to a closed system. Then

$$\Delta p/\Delta T = -\alpha_{12}\rho/\alpha_{11}T. \tag{4}$$

The coefficient α_{12}/α_{11} is readily obtained from (2), taking into account the Onsager relation $\alpha_{12} = \alpha_{21}$:

$$\alpha_{12}/\alpha_{11} = I_Q\big|_T / I_M\big|_T\,. \tag{5}$$

Consequently,

$$\Delta p/\Delta T = -\left.\frac{I_Q}{I_M}\right|_T \frac{\rho}{T}. \tag{6}$$

The isothermal heat flux in the capillary $I_Q \big|_T$ for sufficiently slow flows, taking into account heat transfer in the wall layer, as was shown in (^{1}), is equal to

$$I_Q \big|_T = 1.52\nu\pi R^2 \operatorname{grad} p, \tag{7}$$

where $\operatorname{grad} p = \Delta p/L$, and $\nu = \eta/\rho$ is the kinematic viscosity of the gas.

To determine the flux of matter in the capillary at constant temperature $I_M \big|_T$ in the intermediate region $0.01 \ll \mathrm{Kn} \ll 0.1$ (the slip-flow region), it is necessary to determine the gas transport velocity by means of the Navier–Stokes equation:

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dv}{dr}\right) = -\frac{1}{\eta}\operatorname{grad} p \tag{8}$$

with boundary conditions

$$v \big|_{r\to 0} < \infty, \qquad v \big|_{r=R} = -C_m\lambda\frac{dv}{dr}\bigg|_{r=R}, \tag{9}$$

where C_m is a coefficient equal to 1.09 for complete diffuse reflection of gas molecules from the capillary walls (^{20}).

The solution of equation (8) with boundary conditions (9) has the form

$$v = \left[-r^2 + R^2\left(1 + \frac{2C_m\lambda}{R}\right)\right]\frac{\operatorname{grad} p}{4\eta}. \tag{10}$$

The amount of matter transported by the gas per unit time through the capillary cross section will be equal to

$$I_M \big|_T = -\frac{\pi R^4}{8\nu}\left(1 + \frac{4C_m\lambda}{R}\right)\operatorname{grad} p. \tag{11}$$

Substituting (7) and (11) into (6), we obtain

$$\frac{\Delta p}{\Delta T} = \frac{12.2\eta\nu}{R^2 T}\left(1 + \frac{4C_m\lambda}{R}\right). \tag{12}$$

This formula is applicable under the condition

$$4C_m\lambda/R \ll 1, \tag{13}$$

and also for small values of $\Delta T/T$ and $\Delta p/p$. For convenience in comparison with experimental data, formula (12) can be represented in the form

Fig. 1

Figure 1: Fig. 1

$$\frac{\Delta p}{p} = \frac{12.2\eta^2 R_0}{p\mu R^2}\left[\frac{1}{1+\frac{4C_m\lambda_0}{RP}\left(\frac{T}{T_0}\right)^{n+1}}\right], \tag{14}$$

where R_0 is the universal gas constant, and μ is the molecular weight of the gas.

In writing (14) we have taken into account the dependence of the mean free path of gas molecules on pressure and temperature (^{2})

$$\lambda = \lambda_0 T^{n+1}/pT_0^{n+1},$$

where n is a constant, different for different gases. Formula (14) differs from the corresponding formula of B. V. Derjaguin and S. P. Bakanov ^{1} by the presence in the denominator of a term that depends linearly on C_m and takes into account gas slip. It should be noted that the formula of B. V. Derjaguin and S. P. Bakanov, at low pressures below 7 mm Hg, poorly describes Knudsen’ s experimental data for hydrogen ^{3}. This indicates the need to take into account the gaskinetic jump of velocity at the capillary surface, expressed in the second boundary condition (9). To obtain a formula by which the thermomolecular effect could be calculated over a broad range of temperatures and pressures, it is necessary to integrate (13) over the range of values $p_1 - p_2$ and, respectively, $T_1 - T_2$. If the dependence of viscosity on temperature is used ^{2}

Fig. 1

$$\eta = \eta_0\left(\frac{T}{T_0}\right)^{n+1/2}, \tag{15}$$

then (14) can be represented in the form

$$\frac{dp}{dT} = \frac{12.2\eta_0^2 R_0}{p\mu R^2}\left(\frac{T}{T_0}\right)^{2n+1}\left[\frac{1}{1+\frac{4C_m\lambda_0}{Rp}\left(\frac{T}{T_0}\right)^{n+1}}\right]. \tag{16}$$

Integration of equation (16) is carried out after rather cumbersome, although elementary, calculations. As a result we obtain

$$\lg\frac{p_2}{p_1}=\frac{1}{2}\lg\left|\frac{1-\gamma_1+\dfrac{4C_m\lambda_1}{R}}{1-\gamma_2+\dfrac{4C_m\lambda_2}{R}}\right|+\frac{1}{2}\frac{\beta}{\sqrt{4\alpha+\beta^2}}\lg\left|\frac{u+w}{u-w}\right|, \tag{17}$$

where

$$\gamma_{1,2}=\frac{12.2\eta_0^2R_0T_0}{(1+n)\mu\lambda_0^2}\left(\frac{\lambda_{1,2}}{R}\right)^2;$$

$$\alpha=\frac{12.2\eta_0^2R_0}{(1+n)\mu R^2T_0^{2n+1}};\qquad \beta=\frac{4C_m\lambda_0}{RT_0^{n+1}};$$

$$u=\left(1+\beta\frac{\delta_1+\delta_2}{2\delta_1\delta_2}-\frac{\alpha}{\delta_1\delta_2}\right);\qquad \delta_1=\frac{p_1}{T_1^{n+1}};$$

$$\delta_2=\frac{p_2}{T_2^{n+1}};\qquad w=\sqrt{4\alpha+\beta^2}\left(\frac{\delta_1-\delta_2}{2\delta_1\delta_2}\right).$$

To compare the theory presented with experiment, we used first of all Knudsen' s experimental data for oxygen. In Fig. 1 the theoretical dependence of Δp on p is presented in the pressure interval from 3 to 739 mm Hg, calculated according to formula (17). The dashed line gives the dependence according to Maxwell' s formula. It should be noted that in the pressure interval from 23 to 739 mm, formula (17) gives results very close to the data obtained from the Derjaguin-Bakanov formula, owing to the extremely small value of $4C_m\lambda/R$. At pressures below 23 mm, formula (17) gives results considerably closer to the experimental ones,

than the Deryagin-Bakanov formula, since at lower pressures the influence of gas slip at the capillary walls becomes significant. It should be noted that we did not restrict ourselves to calculations by formula (17) with the value $n=0.314$ specified for oxygen. To verify the results obtained, as well as the validity of the choice of the constant $n=0.314$, we carried out numerical integration of formula (14) for oxygen, taking into account the experimental dependence of the viscosity coefficient on temperature in the temperature interval of Knudsen' s experiment (from 50 to 380° K). It turned out that the results of calculations by formula (17) and of numerical integration of formula (14) differ by no more than 6%.

Calculations based on the Maxwell formula, as is seen from Fig. 1, cannot in any way explain the experimental data in this pressure interval.

At very low pressures from 2 to 0.3 mm, formula (17) was compared with experimental data for nitrogen. As is seen from Fig. 2, the theoretical results

Fig. 2

Figure 2: Fig. 2

according to formula (17) (solid curve) agree considerably better with the experimental data than the results obtained from the Maxwell formula (dashed curve).

Fig. 2

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Received
26 III 1964

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Note: Figure translations are in progress. See original paper for figures.