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The Exchange Efficiencies of the Translational and the Internal Energy of Gas Molecules on Solid Surfaces I. Measurement by Means of Molecular Beams

By

Nobuji Sasaki, Kazuhiko Taku and Kazuo Mitani

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The energy necessary for the thermal reaction must be carried away from the vessel wall by the cold molecules admitted therein, but, in general, they do not come into thermal equilibrium with the wall by a single collision.[1] The attainment of the state of complete thermal equilibrium might finally be brought about by a mere succession of collisions with the wall. But it may be assisted by the intervention of the mutual collision between gas molecules, for it can average *a priori* very plausible differences in α's for various degrees of freedom of the molecule. Such a view may greatly be supported from the chemical side by a fact previously observed in our laboratory. Namely, the nitrogen pentoxide molecules reserved at 0° C could pass almost undecomposed through a 1 m long glass tube of 3 mm diameter at 100° C and at about 10^{-5}mm Hg, although a simple calculation shows that the molecules could have attained 94° C even with an assumption of impossibly poor exchange efficiency ($\alpha = 0.001$), for it will make as many as about 3000 collisions with the wall during its about 1 sec stay inside the tube. This striking stability may be explained by the extreme difficulty of energy transfer from the wall to the degrees of freedom responsible for the decomposition of the molecule if left alone without mutual collisions. On the other hand, there is every reason to assume that the exchange of the translational energy is almost complete and consequently the actual value of α, though not yet measured, must

1. The efficiency of this energy exchange may be measured by Knudsen's accommodation coefficient α defined by

$$\alpha = \frac{T_2 - T_0}{T_1 - T_0},$$

where T_0 and T_2 are the temperatures of the gas molecules before and after the collision with the wall kept at a temperature T_1. The actual value of α lies rarely below 0.1 and generally increases with the increase of the atomic or the molecular weight.

be much larger than that assumed above, even if all other degrees of freedom had zero exchange efficiency. The knowledge of a for different degrees of freedom is in the chemical kinetics interesting as well as important. Attempts to measure separately the accommodation coefficients for the translational (a_t) and the internal energy (a_i) are not lacking but they are either incomplete or too special.[2] Our method would find general application.

A torsion balance with a mirror M in a vacuum, has a vertically stretched thin metallic ribbon R at T_0 as its one wing, against whose surface gas molecules at T_0 almost perpendicularly collide in a form of horizontal molecular beams to deflect the balance by an angle θ_1. Now the ribbon alone is heated to T_1. The deflection increases from θ_1 to θ_2. If n is the number of gas molecules which impinge on the ribbon per unit time, m the mass of a gas molecule and $\bar{c}_0$ the mean velocity of the gas molecules at T_0, the momentum given to the ribbon per unit time is $am\bar{c}_0 n$, where a is the correction factor for oblique collisions made by the molecules in the diverging beams. The momentum given to the ribbon per unit time by the n rebounding molecules is $bm\bar{c}_0 n$ when the ribbon is at T_0 and $bm\bar{c}_2 n$ when at T_1, where b is the correction factor for the molecules being reflected according to the cosine law, and $\bar{c}_2$ the mean velocity of the molecules leaving the surface maintained at T_1. Hence the total momentum given to the ribbon per unit time is

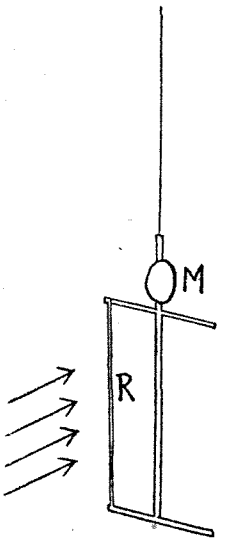

Fig. 1

$$M_1 = am\bar{c}_0 n + bm\bar{c}_0 n,$$

when the temperatures of the gas and the ribbon are T_0, and

$$M_2 = am\bar{c}_0 n + bm\bar{c}_2 n,$$

when the temperature of the gas is T_0 and that of the ribbon T_1.

As M_1/M_2 is equal to θ_1/θ_2, we have

$$\bar{c}_2 = \left\{\left(\frac{a}{b} + 1\right)\frac{\theta_2}{\theta_1} - \frac{a}{b}\right\}\bar{c}_0. \quad \cdots\cdots(1)$$

2. M. Knudsen: Ann. Phys., **6** (1930), 129.
W. R. v. Wijk: Z. Phys., **75** (1932), 584.
L. S. Ornstein and W. R. v. Wyk: Z. Phys., **78** (1932), 734.
H. H. Rowley and K. F. Bonhoeffer: Z. phys. Chem., B **21** (1933), 84.

If the Maxwell's law for the distribution of velocities holds for the departing molecules,

$$(\overline{c_2}/\overline{c_0})^2 = \overline{c_2^2}/\overline{c_0^2} ,$$

where $\overline{c_0^2}$ and $\overline{c_2^2}$ are the mean square velocities of the molecules before and after the collision. Hence we get

$$a_t = \frac{\overline{c_2^2} - \overline{c_0^2}}{\overline{c_1^2} - \overline{c_0^2}} = \frac{\{(a/b + 1)\theta_2/\theta_1 - a/b\}^2 \overline{c_0^2} - \overline{c_0^2}}{\overline{c_1^2} - \overline{c_0^2}} ,$$

or substituting $\overline{c_0^2} = 3RT_0/M$ and $\overline{c_1^2} = 3RT_1/M$, finally,

$$a_t = \frac{[\{(a/b + 1)\theta_2/\theta_1 - a/b\}^2 - 1]T_0}{T_1 - T_0} . \quad \cdots\cdots\cdots\cdots(2)$$

The correction factors a and b can be calculated from the geometry of the ribbon and the defining slits for the beams.

To obtain a_i significant for comparison, we at once measure the total loss of heat E cal per sec from one and the same ribbon heated *in situ* in the gas at p mm Hg. The kinetic theory of gases enables us to calculate a_i from E and a_t by

$$a_i = \frac{17.141 \frac{\sqrt{T_0}M}{pA} E - 3.9738\, a_t (T_1 - T_0)}{(H_1 - H_0) - 2.9804 (T_1 - T_0)} , \quad \cdots\cdots\cdots\cdots(3)$$

where A : the surface area of the ribbon in cm^2, compensated for the end effect,

M : the molecular weight of the gas,

H_0, H_1 : the heat contents of the gas at T_0 and T_1 respectively.

To ensure the frictionless deflection in the actual measurement, the ribbon was heated as a part of a closed circuit with a high frequency resonance coil L_1 and a condensor C in series, all built up in the torsion balance, the heating current being induced from outside. The temperature or the resistance of the ribbon was measured by connecting the two free ends of the ribbon-compensator (by raising the levels in the mercury contacts H in the vacuum) and its middle junction point M (via the suspension wire), with the outside circuit through three choke coils L_2, L_3 and L_4 to form a very weak direct current Wheatstone bridge (Fig. 2).

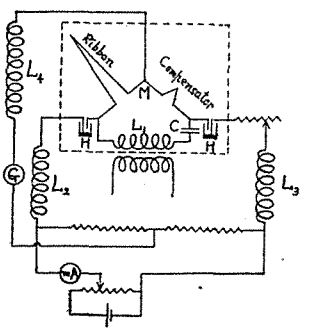

Fig. 2

The results obtained with nitrogen at 31.3° C and a nickel ribbon at 518.0° C are

$$\alpha_t = 0.393 \quad \text{and} \quad \alpha_i = 0.314 \ ,$$

indicating a more efficient exchange for the translational energy in conformity with the results already obtained by other investigators.

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Laboratory of Inorganic Chemistry,
Institute of Chemistry,
College of Science, Kyoto University.