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Measuremets of the Thermal Transpiration Effects of NO at 90 K and of CO, N_2, O_2, CH_4, and He at 77 K

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Synopsis. The thermal transpiration effect of the title gases was measured by a relative method by using a diaphragm-type pressure transducer. The data fit the Takaishi-Sensui equation $[P_1/P_2=(AX^2+BX+C\sqrt{X}+\sqrt{T_1/T_2})/AX^2+BX+C\sqrt{X}+1)]$ quite well in the region of X $(=P_2d_2)$ higher than 0.03 mmHg mm. The values for A, B, and C are 25.5, 9.3, and 0.6 for NO at 90 K, 28.5, 10.5, and 0.6 for CO and N_2, 24.0, 9.2, and 0.8 for O_2, 44.0, 11.4, and 1.2 for CH_4, and 2.96, 0.6, and 1.6 for He at 77 k respectively. The values for the temperature-independent constants, A^*, B^*, and C^* deduced from the values for A, B, and C above, were in agreement with the literature values and/or the estimated values.

In studies of the physical adsorption of nitric oxide and carbon monoxide gases,[1] we measured the thermal transpiration effect[2] of NO and CO. Since no data for the thermal transpiration effect of NO and CO are available in the literature, it may be worthwhile to report our data in detail. To check the reliability of our measuring system, other common gases, N_2, O_2, He, and CH_4, were also studied, and the results were compared with existing data.

Experimental

The nominal purities of N_2, He, O_2, CO, NO, and CH_4 were 99.999, 99.99, 99.9, 99.9, 99.9, and 99.9% respectively. NO was further purified by a method described elsewhere.[1]

The thermal transpiration value, P_1/P_2, was obtained as a function of log P_2d_2 by the relative method. The apparatus used is shown schematically in Fig. 1, where the meanings of P_1, P_2, d_2, *etc.* are illustrated. The pressure difference, P_2-P_3, was measured by means of a Datametrics Barocell Pressure sensor-Electronic Manometer. Then, P_3 was determined by evacuating the chamber, B_2, of the pressure sensor to 10^{-5} Torr. P_2 was calculated from the $P_2=P_3+(P_2-P_3)$ relation. Finally, P_1 was determined from P_3 by the usual method.[3,4] The temperature on the lower side was held at 90 K for NO, and at 77 K for the other gases. The temperature on the higher side was always held at 300 ± 1 K. The pressure region extended down to 2×10^{-2} Torr.

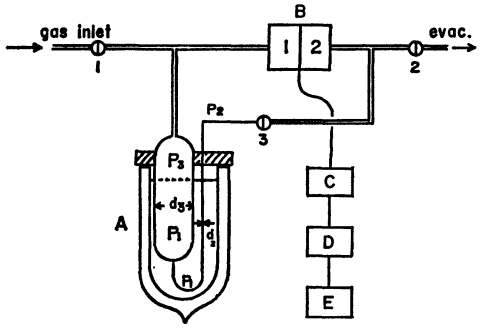

Fig. 1. Schematic representation of the measuring apparatus.
A: Measuring cell, $d_3=46.5$ mm, $d_2=1.45$ mm.
B: Datametrics Barocell Pressure Sensor 570D.
C: Datametrics Barocell Electronic Manometer 1173.
D: Takeda Riken Integrating Digital Voltmeter. TR 66150.
E: Hitachi Recorder 056.

The pressure indication of the electronic manometer was calibrated by the gas-expansion method. The accuracy was within 0.2% at pressures above 1 Torr, within 1.2% between 1 and 0.1 Torr, and within 3% between 0.1 and 0.02 Torr.

Results and Discussion

The P_1/P_2 and P_3/P_2 values of NO measured at 90.5 K are plotted against log P_2d_2 in Fig. 2. The curves for CO and other gases were obtained at 77.5 K, but are not shown in the present paper.

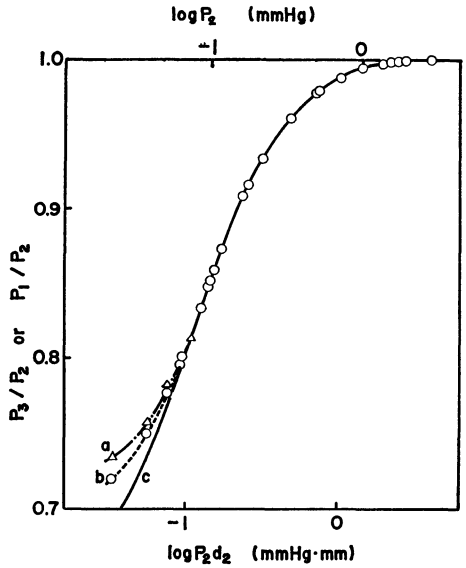

Fig. 2. Plots of thermal transpiration values of NO at 90.5 K.
a: Observed P_3/P_2 *vs.* log P_2d_2,
b: observed P_1/P_2 *vs.* log P_2d_2,
c: calculated P_1/P_2 *vs.* log P_2d_2.

Takaishi and Sensui have proposed the following empirical equation for the thermal transpiration effect:[5]

$$\frac{P_1}{P_2}=\frac{AX^2+BX+C\sqrt{X}+\sqrt{T_1/T_2}}{AX^2+BX+C\sqrt{X}+1} \qquad T_1<T_2, \quad (1)$$

where A, B, and C are constants and where X is P_2d_2. By substituting the experimental data into the equation, the best-fitting values for A, B, and C have been obtained as summarized in Table 1. The degree of their fitness can be seen from Fig. 2.

Table 1. Values[a] for the constants, A, B, and C, contained in the Takaishi-Sensui equation 1, the viscosity coefficient,[b] and the collision diameter[c]

	A (mmHg mm)$^{-2}$	B (mmHg mm)$^{-1}$	C (mmHg mm)$^{-1/2}$	$10^6\eta$ (poise)	D (Å)
NO	25.5	9.3	0.6	179	3.67
CO	28.5	10.5	0.6	166	3.75
N_2	28.5	10.5	0.6	166	3.75
O_2	24.0	9.2	0.8	192	3.60
CH_4	44.0	11.4	1.2	102	4.26
He	2.96	0.6	1.6	186	2.23

a) Values at 90.5 K for NO and those at 77.5 K for other gases. b) Values at 0 °C. "Kagaku Binran," Chemical Society of Japan, p. 470. c) Values calculated from η (see text).

Takaishi and Sensui have demonstrated that the constants, A, B, and C can be written as:

$$A^* = A \times \bar{T}^2, \quad (2)$$

$$B^* = B \times \bar{T}, \quad (3)$$

$$C^* = C\sqrt{\bar{T}}, \quad (4)$$

where $\bar{T}$ is $(T_1+T_2)/2$ and where A^*, B^*, and C^* are the temperature-independent constants. The determined values for A^*, B^*, and C^* are summarized in Table 2 and compared with the literature values. Since no literature values for NO and CO are available, another way of comparison must be made. The A^*, B^*, and C^* constants of NO and CO are estimated from the following Takaishi-Sensui equations:[5,6]

$$\log A^* = 0.507D + 4.146, \quad (5)$$

$$\log B^* = 0.607D + 0.663, \quad (6)$$

$$C^* = (110/D) - 14. \quad (7)$$

Here, D represents the collision diameter of the gases and is calculated from the viscosity coefficient, η, by the aid of $\eta=5\sqrt{\pi mkT}/16\pi D^2$ relation. By using the values of D summarized in Table 1, the values for A^*, B^*, and C^* are calculated. The results are summarized in Table 2. The agreement between the observed values for the constants and the literature and/or estimated values is reasonably good for all of the gases measured.

Table 2. Constants, A^*, B^*, C^*, contained in Eqs. 2—7

		$10^{-5}A^*$ (deg/mmHg mm)^2	$10^{-2}B^*$ (deg/mmHg mm)	C^* (deg/mmHg mm)$^{1/2}$
NO	obsd	9.7	18	9
	calcd	10	7.8	16
CO	obsd	10	20	8
	calcd	11	8.7	15
N_2	obsd	10	20	8
	lit	12	10	10—18
	calcd	11	8.7	15
O_2	obsd	8.6	17	10
	lit	9—7	16—19	—
	calcd	9.4	7.1	17
CH_4	obsd	16	22	16
	lit	15	15	13
	calcd	20	12	12
He	obsd	1.1	1.1	22
	lit	1.4—1.6	1.2—1.1	18—20
	calcd	1.9	1.0	35

obsd: observed value in the present work. lit.: literature value summarized in Ref. 5. calcd: calculated value in the present work (see text).

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5) T. Takaishi and Y. Sensui, *Trans. Faraday Soc.*, **59**, 2503 (1963).
6) The original equations used to estimate A^* and B^* in Ref. 5 are incorrect. They must be corrected to Eqs. 5 and 6 of the present paper.