THERMOMOLECULAR EFFECT OF GAS MIXTURES

J.ADÁMEK

Department of Physical Chemistry,
Charles University, Prague 2

Thermomolecular effect of a gas mixture can be described by the Liang equation. Individual components contribute to the resulting effect additively according to their concentration in the mixture.

Manometric measurements performed with a gas in a closed system where a temperature gradient exists must be usually corrected at lower pressures than a few Torr for the thermomolecular effect. The calculation of the pressure difference established between unequally warm parts of such a system can be made with the use of the Liang equation[1-12].

Up to now, however, gas mixtures have not been studied; such cases are frequently met in various kinetic or gas adsorption measurements. In the present work the use of the Liang equation was extended to gas mixtures.

EXPERIMENTAL

Measurements were made by the relative method[1] on a vacuum apparatus described in preceding communications[10-12]. Two helium–xenon mixtures and one xenon–krypton mixture were used as model systems. The gases were obtained from commercially available ampoules and were of spectral purity. Prior to letting into the apparatus, the gases were purified by the usual method[10-12]. The inner diameter of the capillary arm of a U-shaped vessel used was 1·58 mm, that of the wide arm 60 mm.

During the measurement, a certain amount of a gaseous mixture was injected into the evacuated measuring compartment. After a certain time when a stationary state was attained, the pressures p_1 and p_2 corresponding to the parts of the system maintained at temperatures T_1 and T_2 were determined. The ratio p_1/p_2 was plotted as function of p_2.

After the measurement with one gaseous sample was finished, the measuring compartment was evacuated to 10^{-6} Torr and another sample was injected. A given gas mixture was in turn subjected to measurements in the range from units to thousandths of a Torr.

RESULTS

In Fig. 1 are shown the dependences of p_1/p_2 on log p_2 measured for pure components of the corresponding mixtures; Fig. 2 shows the same dependences for the mixtures. In addition, the measured values are compared with those calculated from the Liang equation. The Liang curves were calculated for pure components according to

$$\frac{p_1}{p_2} = \frac{\alpha_{He}X^2\varphi_g^2 + \beta_{He}X\varphi_g + R_m}{\alpha_{He}X^2\varphi_g^2 + b_{He}X\varphi_g + 1} , \qquad (1)$$

where $X = p_2 D$, $R_m = (T_1/T_2)^{1/2}$, D denotes diameter of the capillary arm of the U-shaped vessel in mm, T_1 and T_2 are absolute temperatures of the tempering bath and of the laboratory, respectively, p_1 and p_2 pressures in Torr, α_{He}, β_{He}, φ_g constants of the Liang equation. The following values were used: $\varphi_{He} = 1$, $\varphi_{Kr} = 3\cdot9$, $\varphi_{Xe} = 6\cdot41$, $\alpha_{He} = 0\cdot85$ for $T_1 = 473$ K and 0·48 for 573 K, $\beta_{He} = 1\cdot79$ for $T_1 = 473$ K and 2·09 for 573 K.

The Liang curves for mixtures were calculated in two ways. The full curve in Fig. 2 corresponds to the equation

$$R_s = R_A x_A + R_B x_B , \qquad (2)$$

where x_A and x_B denote mole fractions of components A and B in their mixture, R_A and R_B values of p_1/p_2 calculated from Eq. (1) for components A and B at the conditions of measurement, R_s value of p_1/p_2 for the mixture.

The other method of calculation (dashed curve in Fig. 2) is also based on the Liang equation (1), where the unknown φ_g value for the mixture was determined as
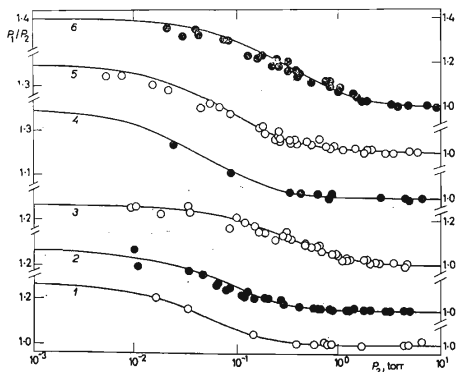

Fig. 1

Thermomolecular Effect of Xenon, Krypton and Helium

Dependence of p_1/p_2 on p_2 (Torr). $T_1 = 474$ K: 1 Xe, 2 Kr, 3 He; $T_1 = 573$ K: 4 Xe, 5 Kr, 6 He; $T_2 = 293$ K, $D = 1\cdot58$ mm. Circles denote experimental points, full curve is calculated.

$$\varphi_s = \varphi_A x_A + \varphi_B x_B. \tag{3}$$

Here φ_A, φ_B and φ_s denote values of φ_g for the components A and B and for their mixture.

The measured p_1 and p_2 values in logarithmic coordinates are plotted in Fig. 3 for all mixtures under consideration.

DISCUSSION

It is obvious from the results that the Liang equation (1) can be well used even for gas mixtures. The measured and calculated values of p_1/p_2 are in good accord, the deviations in the case of mixtures being approximately the same as those observed with pure components (Figs 1 and 2).

In the calculation of Liang curves for pure components according to Eq. (1), the α_{He} and β_{He} values found earlier[11] and the tabulated φ_g values[5] were used (full lines in Fig. 1). The Liang curves for the mixtures were calculated by two methods from Eqs (2) and (3), both involving the assumption that the Liang equation holds and
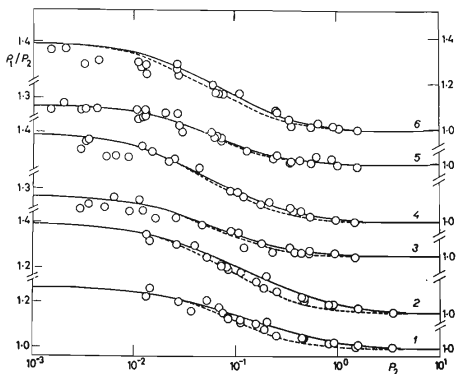

Fig. 2

Thermomolecular Effect of Gas Mixture

Dependence of p_1/p_2 on p_2 (Torr). *1* and *2* 473 and 573 K, respectively, $x_{Xe} = 0.48$, $x_{He} = 0.52$; *3* and *4* $T_1 = 473$ and 573 K, respectively, $x_{Xe} = 0.87$, $x_{He} = 0.13$; *5* and *6* $T_1 = 473$ and 573 K, respectively, $x_{Xe} = 0.54$, $x_{Kr} = 0.46$. $T_2 = 293$ K, $D = 1.58$ mm. Circles denote experimental points; full curve is calculated.

that the components behave independently. It is seen from Fig. 2 that a better agreement with the measured values is attained by the first method using Eq. (2). However, both methods are suitable since differences between the curves calculated for a given mixture from Eqs (2) and (3) are about as large as experimental errors observed with pure components.

Both methods of calculation of Liang curves for a mixture prove not only that the Liang equation applies for gas mixtures but also that the influences of individual components are additive. The components participate on the total thermomolecular effect of the mixture independently of each other according to their mole fraction.

The dependences of the measured pressures p_1 on p_2 in logarithmic coordinates are linear (Fig. 3). In these coordinates only one linear dependence for all mixtures under study was obtained independent of the temperature of measurement T_1. The same straight line corresponds also to the dependence of the measured pressures p_1 on p_2 for pure components. (In Fig. 3 are shown for simplicity only the values for mixtures.) It seems that there is a close relationship with equations derived by Knudsen[13] and independently by Weber[14]:

$$p_1/p_2 = (T_1/T_2)^{1/(2+k/\lambda)}, \tag{4}$$

where k is a numerical factor involving the size of the capillary tube with a temperature gradient, and λ denotes mean free path of a molecule of the gas under consideration.
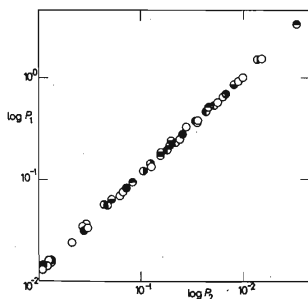

FIG. 3

Thermomolecular Effect of Gas Mixture

Dependence of p_1 on p_2 in logarithmic coordinates. ◑ and ◐ $T_1 = 473$ and 573 K, respectively, $x_{Xe} = 0.48$, $x_{He} = 0.52$; ◑ and ◐ $T_1 = 473$ and 573 K, respectively, $x_{Xe} = 0.87$, $x_{He} = 0.13$; ○ and ● $T_1 = 473$ and 573 K, respectively, $x_{Xe} = 0.54$, $x_{Kr} = 0.46$. $T_2 = 293$ K, $D = 1.58$ mm.

CONCLUSIONS

The thermomolecular effect of a gas mixture can be described by the Liang equation on the assumption that the components participate on the overall effect independently of one another according to their concentration. The dependence of the measured pressures p_1 on p_2 in logarithmic coordinates is linear for all mixtures and independent of the temperature of measurement.

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