Influence of Pressure on Thermal Diffusion in Binary and Ternary Mixtures of Helium, Nitrogen, and Neon

Lawrence E. Ita[1] and Richard E. Sonntag[2]

Department of Mechanical Engineering, University of Michigan, Ann Arbor, Mich. 48104

The influence of pressure on separation in binary and ternary gaseous systems involving nitrogen, helium, and neon was studied in a conventional two-bulb apparatus. The low bulb temperatures studied were 120, 140, and 160K, and the high bulb temperature was 273K. The pressure range investigated was 3–40 atm, and composition measurements were made with a mass spectrometer. The experimental results indicated that the nitrogen–helium separation in a ternary system with neon is less than that for the nitrogen–helium binary system at the same operating conditions. Separation increased with pressure for both cases. In the neon–helium binary system, separation was not affected by pressure, and the corresponding separation for the ternary system with nitrogen as third component exceeded the binary separation above a pressure value which increased with the low bulb temperature.

The possibility of increasing separation in thermal diffusion systems is of continuing interest. Variation of pressure in some earlier measurements produced no observable influence on separation (3, 7). However, the range of pressure variation was small, and gases were studied at conditions which approximate ideal behavior. Later measurements by Becker (7) and VanEe (11) indicated that pressure influence could be considerable.

The Chapman-Enskog theory of transport properties predicts no pressure influence on thermal diffusion. However, Enskog's modification to the kinetic theory of dilute gases, extended to thermal diffusion (2), does predict an effect but orders of magnitude lower than measured values.

A theoretical approach to thermal diffusion from the viewpoint of a coupled flow system by use of the tech-

[1] Present address, University of Nevada, Las Vegas, Nev.
[2] To whom correspondence should be addressed.

niques of linear irreversible thermodynamics has been made previously (6). Correlations with experimental measurements (11) were not entirely satisfactory, however.

The idea of using a third component to "push apart" two other components in a mixture has also received some attention in the literature and is studied here for a nitrogen–helium (neon) system.

Experimental Equipment

The basic test package consists of two copper cells approximately 95 cc in volume, connected by a 1-in. diameter stainless-steel tube. The lower cell was surrounded with $\frac{1}{4}$-W carbon resistors and enclosed in a heat transfer can. Cooling was effected by immersing the can in a cryostat containing liquid nitrogen, and test temperatures were maintained by varying electrical power supplied to the resistors from a temperature controller. The upper cell was immersed in a water–ice mixture to maintain its temperature.

Temperatures on the lower cell were measured by a platinum resistance thermometer with a type G-2 Mueller bridge. Calibrated copper–constantan thermocouples were utilized to check temperature gradients and to measure temperatures on the upper cell and connecting tube.

Each cell contained two 0.004-in. i.d. capillary sampling tubes, and the test samples were collected in evacuated glass bottles. Nearly equal volumes of samples were withdrawn from each tube. Composition analysis was performed on a Bendix TOF mass spectrometer. Pressure in the test cells was measured by a differential pressure indicator and 16-in. calibrated Heise gages.

Experimental Procedure and Results

The test mixture was introduced into the test cell after evacuation to about 20 μ. Rapid cooling was then effected by filling the heat-transfer space with helium gas. The cells were brought to the test temperatures, evacuated, and refilled with fresh mixture to the test pressure.

Table I. Experimental Results for Ternary Mixture of Helium, Neon, and Nitrogen

Mole composition, He (0.336), Ne (0.331), N₂ (0.333)
Upper cell temperature (T_2), 273.0K
Lower cell temperature (T_1)

T_1, K	P, atm	f_{He}	f_{Ne}	$f_{N_2}{}^a$	$f_{He}{}'$	$f_{Ne}{}'$	$f_{N_2}{}'^b$	α (He–Ne) (tern)	α (He–N₂) (tern)
120.0	2.89	0.314	0.339	0.347	0.371	0.320	0.309	0.273	0.344
	20.0	0.310	0.338	0.352	0.383	0.310	0.307	0.362	0.424
	38.8	0.303	0.335	0.362	0.390	0.324	0.296	0.348	0.552
140.0	3.17	0.314	0.335	0.351	0.358	0.318	0.324	0.274	0.316
	20.2	0.318	0.335	0.347	0.373	0.320	0.307	0.307	0.422
	44.5	0.311	0.335	0.354	0.369	0.326	0.305	0.297	0.552
160.0	3.54	0.321	0.334	0.345	0.362	0.324	0.314	0.282	0.401
	22.8	0.319	0.334	0.347	0.365	0.325	0.310	0.303	0.463
	49.7	0.310	0.338	0.352	0.358	0.327	0.315	0.331	0.477

^{a} Mole fraction in lower cell. ^{b} Mole fraction in upper cell.

With experience from extensive test runs, samples were drawn only twice in most runs, the times being chosen to ensure essential attainment of steady state. Typically, samples were drawn 12 and 16 hr after the start of a run.

The following limits of accuracy were maintained in the test runs: internal temperatures in test cells, ±0.1K; pressure, ±1% of the test pressure; and composition, ±0.5 vol %.

The experimental results are given in Tables I–III. In Table I the measured compositions and calculated thermal diffusion factors are given for a ternary mixture of approximately equal proportions of helium, neon, and nitrogen. The same information, as well as percent separation, S, is given for a helium–nitrogen binary of approximately equal proportions in Table II and for the corresponding helium–neon binary in Table III.

Table II. Experimental Results for Binary Mixture of Helium and Nitrogen

Mole composition, He (0.502), N₂ (0.498)
Upper cell temperature (T₂), 273.0K
Lower cell temperature (T₁)

P, atm	T₁, K	f_{He}	f_{He}'	f_{N_2}	f_{N_2}'	S, %	α
3.0	120.0	0.450	0.529	0.540	0.471	7.9	0.363
20.0	120.0	0.435	0.548	0.565	0.452	11.3	0.552
40.0	120.0	0.429	0.569	0.571	0.431	14.0	0.686
3.0	140.0	0.483	0.552	0.517	0.448	6.9	0.414
20.0	140.0	0.462	0.550	0.538	0.450	8.8	0.529
40.0	140.0	0.492	0.599	0.508	0.401	10.7	0.649
3.0	160.0	0.487	0.543	0.513	0.457	5.6	0.420
20.0	160.0	0.483	0.548	0.517	0.452	6.5	0.488
40.0	160.0	0.474	0.546	0.526	0.454	7.2	0.540

Table III. Experimental Results for Binary Mixture of Helium and Neon

Mole composition, He (0.504), Ne (0.496)
Upper cell temperature (T₂), 273.0K
Lower cell temperature (T₁)

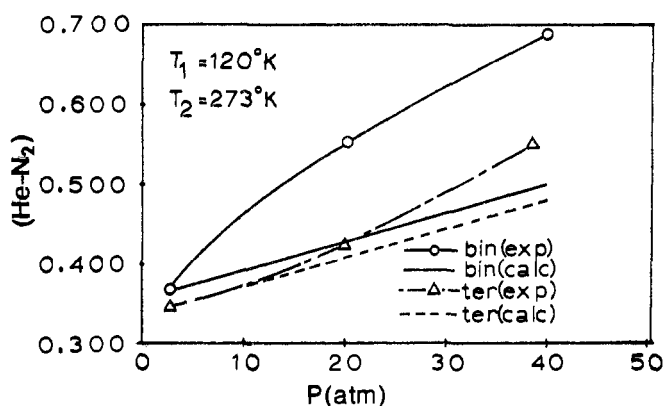| P, atm	T₁, K	f_{He}	f_{He}'	f_{Ne}	f_{Ne}'	S, %	α
3.0–40.0	120.0	0.484	0.545	0.516	0.455	6.1	0.298
3.0–40.0	140.0	0.487	0.538	0.513	0.462	5.1	0.306
3.0–40.0	160.0	0.487	0.529	0.513	0.471	4.2	0.315

Figure 1. Thermal diffusion factor vs. pressure. Binary mixture: He (0.502), N₂ (0.498). Ternary mixture: He (0.336), Ne (0.331), N₂ (0.333)

Discussion of Results

The effect of pressure on He–N₂ thermal diffusion factors is shown in Figures 1–3. The behavior in this system is governed largely by the increasing nonideal behavior of nitrogen as the temperature is decreased. For an increase of test pressure from 3 to 40 atm, the thermal diffusion factor increases by approximately 20% at 160K and 80% at 120K. Percent separation in the He–N₂ bina-
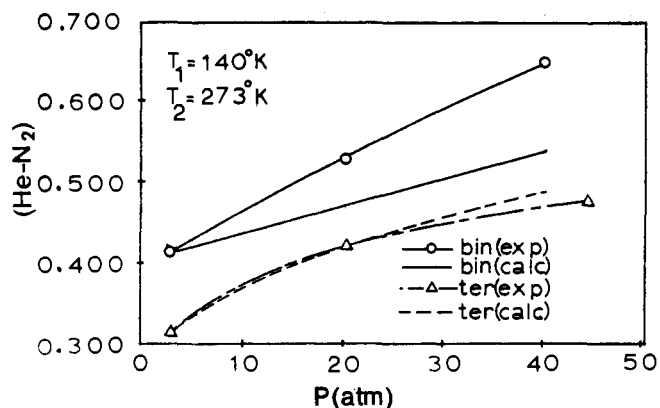

Figure 2. Thermal diffusion factor vs. pressure. Binary mixture: He (0.502), N₂ (0.498). Ternary mixture: He (0.336), Ne (0.331), N₂ (0.333)
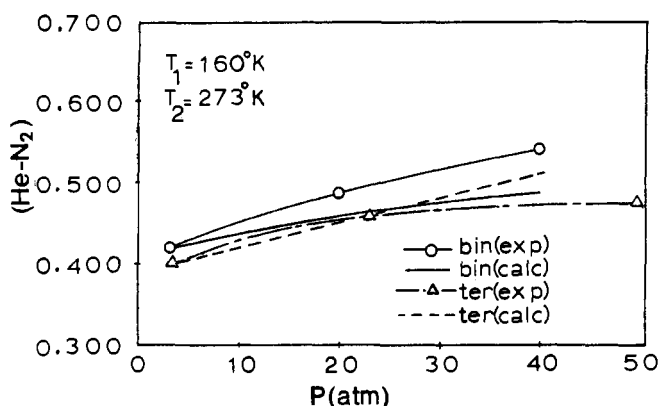

Figure 3. Thermal diffusion factor vs. pressure. Binary mixture: He (0.502), N₂ (0.498). Ternary mixture: He (0.336), Ne (0.331), N₂ (0.333)
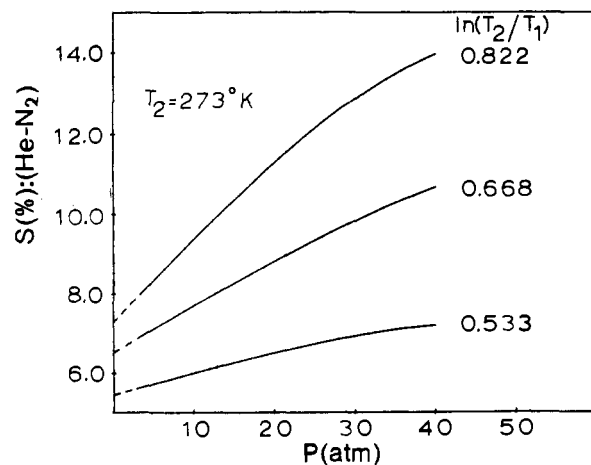

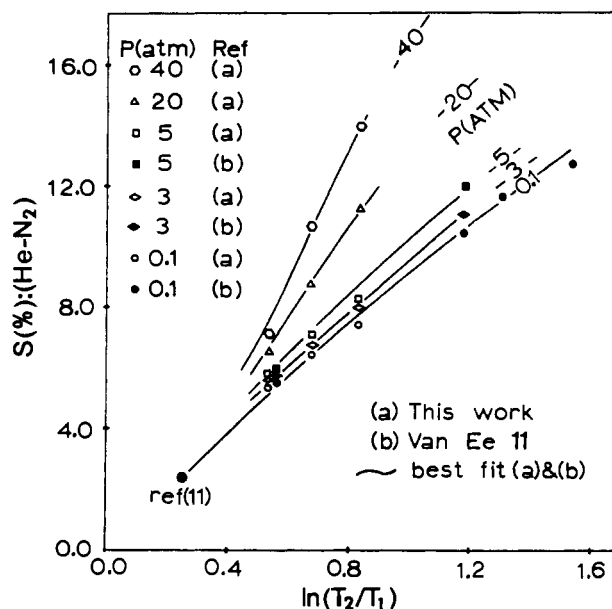Figure 4. Separation vs. pressure. Binary mixture: He (0.502), N₂ (0.498)

Figure 5. Separation vs. $\ln(T_2/T_1)$. Binary mixture: He (0.502), N_2 (0.498)
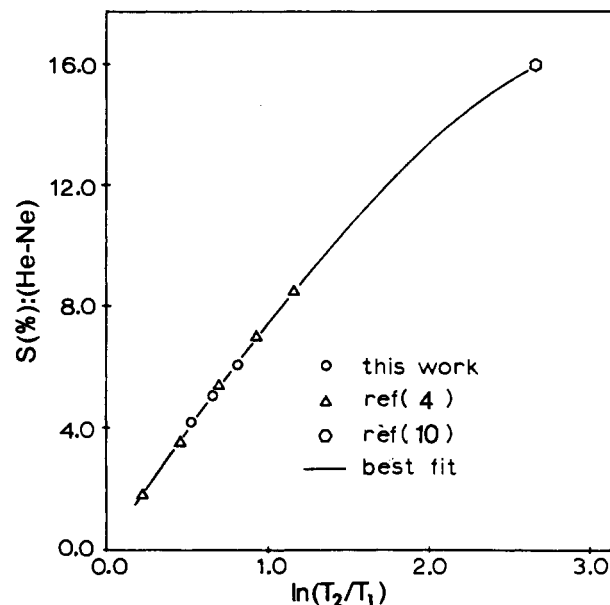

Figure 7. Separation vs. $\ln(T_2/T_1)$. Binary mixture: He (0.504), Ne (0.496)
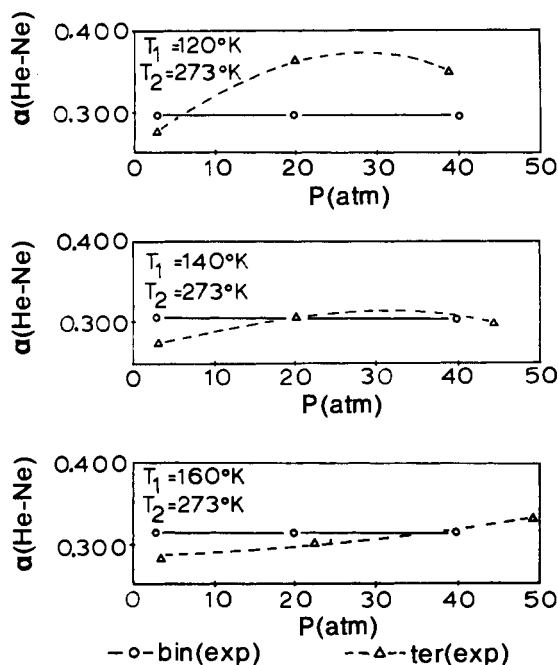

$-o-$ bin(exp) $--\triangle--$ ter(exp)

Figure 6. Thermal diffusion factor vs. pressure. Binary mixture: He (0.504), Ne (0.496). Ternary mixture: He (0.336), Ne (0.331), N_2 (0.333)

ry system as a function of pressure is presented in Figure 4. Comparison of the measurements of this research with those of VanEe (11) (Figure 5) (values at 0.1 and 5 atm by interpolation) indicates a satisfactory agreement.

The lack of pressure dependency of thermal diffusion in the He–Ne binary system is shown in Figure 6. At the temperatures and pressures covered in this investigation, both gases behave nearly ideally. Comparison of these results with those of Grew (4) and Troyer et al. (10) (Figure 7) is also considered to be quite satisfactory (some extrapolation was necessary because of slight composition differences in the mixtures).

In the ternary mixtures, the thermal diffusion factor for He–N_2 is lower than in the binary system. For He–Ne, however, this is true only for certain pressures that de-

pend on the system temperature (Figure 6). Additional measurements would be required to establish conditions under which "pushing apart" may be expected in ternary mixtures.

The theoretical values shown in Figures 1–3 are based on an analytical model developed elsewhere (8). Application of the procedures of irreversible thermodynamics to the steady-state condition in a coupled flow (heat and mass) system results in an expression for pressure dependency of the thermal diffusion factor. The general procedure follows that of previous work (6), but in the present case, the heat of transfer is expressed as the excess enthalpy of the mixture. The result is then given in terms of the mixture equation of state.

The results shown here were calculated from the virial equation, with second and third-virial coefficients calculated by the Lennard-Jones (6–12) potential function. The increased accuracy of correlation for the ternary system over the binary at the same pressure and temperature and for increasing temperature are both attributable to decreased density of the mixture. That is, the two-coefficient virial equation is restricted to low-to-moderate density calculations, and a more accurate equation would be required for the higher densities, such as is the case in the He–N_2 binary at 120 and 140K. It is felt that the accuracy of correlation at the lower densities demonstrates the validity of such a model.

Literature Cited

(1) Becker, E. W., Z. Naturforsch., **5a**, 457 (1950).
(2) Chapman, S., Cowling, T. G., "The Mathematical Theory of Non-Uniform Gases," Cambridge Univ. Press, Cambridge, England, 1958.
(3) Drickamer, H. G., Hofto, J. R., J. Chem Phys., **17**, 1165 (1949).
(4) Grew, K. E., Proc. Roy. Soc., Ser. A, **189**, 402 (1947).
(5) Grew, K. E., Atkins, B. E., Proc. Phys. Soc., **48**, 415 (1936).
(6) Haase, R., Z. Phys., **127**, 1 (1950).
(7) Ibbs, T. L., Grew, K. E., Hirst, A. A., Proc. Phys. Soc., **41**, 456 (1929).
(8) Ita, L. E., thesis, University of Michigan, Ann Arbor, Mich., 1970.
(9) Platten, J., Hamm, J., Thomaes, G., Mousselin, L., Chanu, J., Physica, **42**, 607 (1969).
(10) Troyer, A., van Itterbeek, A., van Den Berg, G. J., ibid., **16**, 669 (1950).
(11) VanEe, H., thesis, University of Leiden, Leiden, The Netherlands, 1966.