ρ = molal density of mixture, (lb. moles total)/(cu. ft.)
σ = $(F_y/F_T)(\eta - 1)(y - y_o)/(T_w - T_o)$
ϕ_C = $h_C/h_C{}^*$
ϕ_E = $h_E/h_B{}^*$
ϕ_F = $h_F/h_B{}^*$
ϕ_H = $h_H/h_B{}^*$
ψ = $(T - T_o)/(T_w - T_o)$

Subscripts

A = species A
E = equilibrium mixing box conditions
i = pipe inlet
o = center line of pipe
ss = steady state, that is not changing with L
V = species V
w = pipe wall
99% = point at which ϵ is 99% of ϵ_{ss}

Superscripts

$*$ = physical heat transfer

LITERATURE CITED

1. Altman, David, and Henry Wise, *J. Am. Rocket Soc.*, **26**, 256 (1956).
2. Brian, P. L. T., and R. C. Reid, *A.I.Ch.E. Journal*, **8**, 322 (1962).
3. Brokaw, R. S., *Natl. Advisory Comm. Aeronaut., Reclassification Notice, E57k19a* (March, 1958).
4. ———, *J. Chem. Phys.*, **35**, 1569 (1961).
5. Corrsin, Stanley, *Phys. Fluids*, **1**, 42 (1958).
6. Deissler, R. G., *Natl. Advisory Comm. Aeronaut. Rept. 1210* (1955). Reproduced in reference 9, pp. 253-280.
7. Fay, J. A., and F. R. Riddell, *J. Aeronaut. Sci.*, **25**, 73 (1958); *Res. Rept. No. 1*, Avco Corporation, Everett, Massachusetts (April, 1957).
8. Furguson, R. R., and J. M. Smith, *A.I.Ch.E. Journal*, **8**, 654 (1962).
9. Hartnett, J. P., ed., "Recent Advances in Heat and Mass Transfer," McGraw-Hill, New York (1961).
10. Irving, J. P., and J. M. Smith, *A.I.Ch.E. Journal*, **7**, 91 (1961).
11. Krieve, W. F., and D. M. Mason, *ibid.*, p. 277.
12. Lees, Lester, *Jet Propulsion*, **26**, 259 (1956).
13. Martinelli, R. C., *Trans. Am. Soc. Mech. Engrs.*, **69**, 947 (1947).
14. Metzdorf, H. J., *J. Aeronaut. Sci.*, **25**, 200 (1958).
15. Moore, L. I., *ibid.*, **19**, 505 (1952).
16. Richardson, J. L., F. P. Boynton, K. Y. Eng, and D. M. Mason, *Chem. Eng. Sci.*, **13**, 130 (1961).
17. Rose, P. H., R. F. Probstein, and M. C. Adams, *J. Aeronaut. Sci.*, **25**, 751 (1958).
18. Schotte, William, *Ind. Eng. Chem.*, **50**, 683 (1958).
19. Sleicher, C. A., Jr., and M. Tribus, *Trans. Am. Soc. Mech. Engrs.*, **79**, 789 (1957). Reproduced in reference 9, pp. 281-301.
20. Thievon, W. J., G. A. Sterbutzel, and J. L. Beal, *Wright Air Develop. Center. Tech. Rept. 59-450* (June, 1959).
21. Von Kármán, Theodore, *Trans. Am. Soc. Mech. Engrs.*, **61**, 705 (1939).
22. Ziebland, H., *J. Brit. Interplant. Soc.*, **14**, 249 (1955).

Manuscript received January 11, 1963; revision received July 8, 1963; paper accepted July 8, 1963. Paper presented at Heat Transfer Conference, Boston, Massachusetts (1963).

Calculation of Thermal Diffusion Factors for the Methane-n-Butane System in the Critical and Liquid Regions

W. M. RUTHERFORD
Mound Laboratory, Monsanto Research Corporation, Miamisburg, Ohio

Ordinary thermodynamic methods are inadequate for the treatment of steady state, nonequilibrium processes such as thermal diffusion. It is possible however to treat such phenomena by means of the thermodynamics of the steady state, the methods of which have been described by De Groot (*1*) and others (*2, 3*).

Steady state thermodynamic theory, as applied to the thermal diffusion phenomenon, gives a result for the thermal diffusion factor in terms of a single undetermined parameter, the heat of transport. The relationship between the thermal diffusion factor and the heat of transport may take several forms according to the particular choice of the form of the thermodynamic fluxes and forces used in the derivation. In a previous paper (*4*) the author has made use of the expression

$$\alpha = \frac{Q_1{}^{**}}{x_1(\partial \mu_1/\partial x_1)_{T,p}} \tag{1}$$

where α is defined by the following equation for the mass flux of one component of a binary mixture subjected to a temperature gradient:

$$J_1 = \frac{D_{12}M_1\rho}{\overline{M}}\left[\nabla x_1 - \frac{\alpha x_1 x_2}{T}\nabla T\right] \tag{2}$$

$Q_1{}^{**}$ is the heat of transport and is the heat transported per mole of moving molecules of species 1 (in a two-component system) minus the enthalpy transport.

In reference *4* detailed experimental data were reported for thermal diffusion of methane-*n*-butane mixtures in the liquid and critical regions. These data were used to demonstrate the strong dependence of the thermal diffusion factor on the chemical potential derivative $(\partial\mu_1/\partial x_1)_{T,P}$. No attempt was made to interpret or estimate $Q_1{}^{**}$, although it was clear from the experimental results that $Q_1{}^{**}$ is a function of temperature and pressure.

PREDICTION OF THE THERMAL DIFFUSION FACTOR

By another choice of thermodynamic fluxes and forces a different, but equivalent, expression for the thermal diffusion factor can be derived

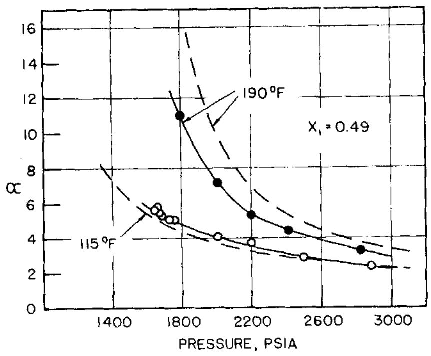

Fig. 1. Calculated and experimental values of the thermal diffusion factor for the methane-*n*-butane system at 115° and 190°F. and 0.49 mole fraction methane. (The dashed curve is calculated.)

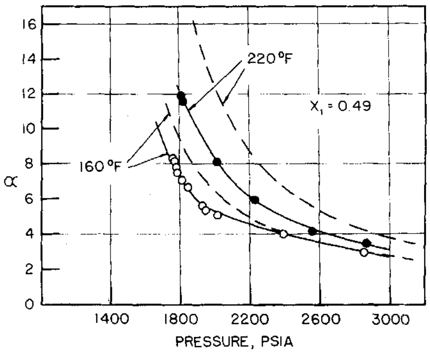

Fig. 2. Calculated and experimental values of the thermal diffusion factor for the methane-*n*-butane system at 160° and 220°F. and 0.49 mole fraction methane.

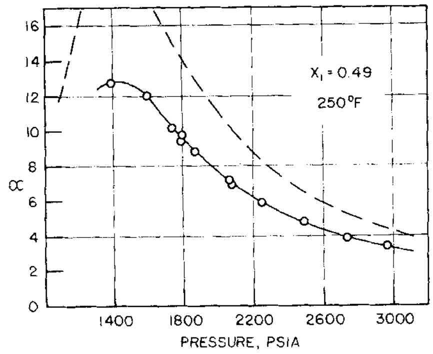

Fig. 3. Calculated and experimental values of the thermal diffusion factor for the methane-*n*-butane system at 250°F. and 0.49 mole fraction methane.

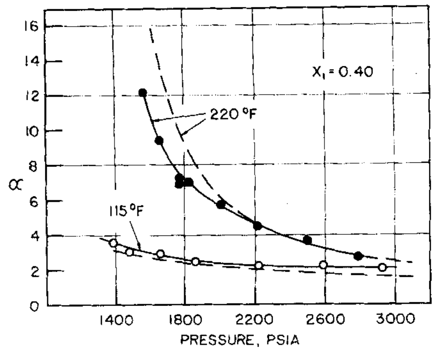

Fig. 4. Calculated and experimental values of the thermal diffusion factor for the methane-*n*-butane system at 115° and 220°F. and 0.40 mole fraction methane.

TABLE 1. CALCULATED VALUES OF α_0 FOR THE METHANE-*n*-BUTANE SYSTEM (FIRST APPROXIMATION)

Temperature, °F.	0.40 mole fraction methane	0.49 mole fraction methane
100	0.0557	0.0594
115	0.0620	0.0661
160	0.0763	0.0814
190	0.0859	0.0916
220	0.0947	0.1009
250	0.1038	0.1107

$$\alpha = \frac{(q_1^* - h_1 + h_2)\, M_1 M_2}{\overline{M}\, x_1 (\partial\mu_1/\partial x_1)_{T,p}} \tag{3}$$

where q_1^* is now a heat of transport which includes the enthalpy transport and refers to unit mass. If one assumes that q_1^* is independent of temperature and pressure, one can write for a gas at infinite dilution

$$\alpha_0 = \frac{(q_1^* - h_{10} + h_{20})\, M_1 M_2}{\overline{M} RT} \tag{4}$$

Now eliminating q_1^* between (3) and (4) one has

$$\alpha = \frac{\alpha_0\, RT}{x_1 (\partial\mu_1/\partial x_1)_{T,P}} + \frac{M_1 M_2 \,[(h_2 - h_{20}) - (h_1 - h_{10})]}{\overline{M}\, x_1 (\partial\mu_1/\partial x_1)_{T,p}} \tag{5}$$

This equation for α, first proposed by Haase (*5*, *6*), contains no undetermined quantities (α_0 can be calculated from kinetic theory). It has been applied with success by Haase to the moderately dense gas data of Becker (*7*, *8*). Robb and Drickamer (*9*) have applied Equation (5) to the ethane-xenon system in the critical region, but the comparison was limited by the lack of precise thermodynamic data for the system.

THERMAL DIFFUSION FACTORS FOR THE METHANE-*n*-BUTANE SYSTEM

Equation (5) has been applied to the experimental conditions of reference *4*. Values of α_0 as a function of temperature were calculated from kinetic gas theory by means of the Lennard-Jones potential. These values appear in Table 1. The intermolecular potential parameters used (*10*) are given in Table 2. Partial specific enthalpies for both components were calculated from the Benedict-Webb-Rubin equation of state (*11*). The chemical potential derivative had been calculated previously from the Benedict-Webb-Rubin equation.

Calculated values of α are plotted in Figures 1 through 5 along with corresponding experimental results from the previous work. Figure 6 is a phase diagram for the methane-*n*-butane system at the two experimental compositions, 0.40 and 0.49 mole % methane.

Agreement between calculated and experimental values of the thermal diffusion factor is quite good. Deviations are within the probable limits of error of the experimental

TABLE 2. INTERMOLECULAR POTENTIAL ENERGY PARAMETERS USED IN THE CALCULATION OF α_0

	methane	*n*-butane
ϵ/k, °K.	137	410
σ, Å	3.882	4.997

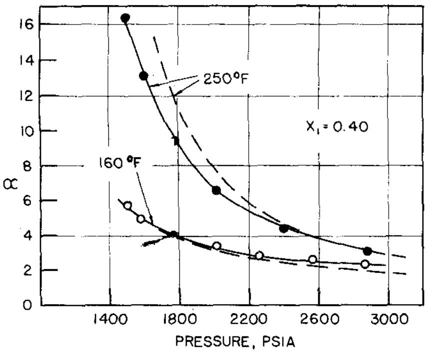

Fig. 5. Calculated and experimental values of the thermal diffusion factor for the methane *n*-butane system at 160° and 250°F. and 0.40 mole fraction methane.

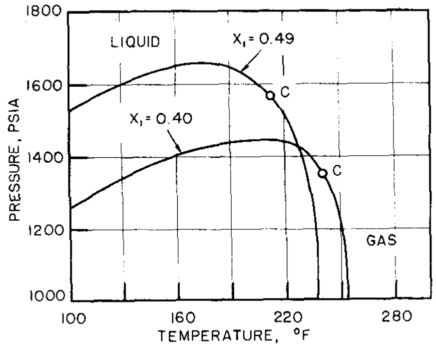

Fig. 6. Phase behavior of the methane-*n*-butane system in the critical region at 0.40 and 0.49 mole fraction methane.

data and of the calculated thermodynamic parameters. The differences between theory and experiment are greatest in the immediate region of the critical point. They become quite small in the liquid regions of the phase diagram. This behavior could be almost entirely the result of uncertainties in the calculated values of the chemical potential derivative, inasmuch as this is a difficult function to evaluate accurately in the critical region.

DISCUSSION

The good agreement between theory and experiment in the liquid regions of the methane-*n*-butane system suggests that Equation (5) may be generally applicable to liquid mixtures. In most cases the term involving α_0 is of negligible magnitude and the thermal diffusion factor is given by

$$\alpha = \frac{M_1 M_2 \left[(h_2 - h_{20}) - (h_1 - h_{10}) \right]}{\overline{M}\, x_1 (\partial \mu_1 / \partial x_1)_{T,p}} \qquad (6)$$

For isotopic mixtures one can assume that the molar enthalpies of the two components are equal

$$H_1 = H_2 \qquad (7)$$

and that

$$x_1 (\partial \mu_1 / \partial x_1)_{T,p} = RT \qquad (8)$$

The thermal diffusion factor for a liquid mixture of isotopes is then

$$\alpha = \frac{(H - H_0)(M_1 - M_2)}{\overline{M} RT} \qquad (9)$$

For isomeric mixtures

$$M_1 = M_2 \qquad (10)$$

and (6) reduces to

$$\alpha = \frac{(H_2 - H_{20}) - (H_1 - H_{10})}{x_1 (\partial \mu_1 / \partial x_1)_{T,p}} \qquad (11)$$

It is a well-established fact that the magnitude of the thermal diffusion effect in liquids depends in part on differences in molecular shape and in part on differences in molecular weight of the two species. It is very satifying therefore to find that this dual dependence comes naturally out of Equation (6) upon consideration of the two extreme cases, isotopes and isomers.

It remains to be seen of course whether the above speculations can be confirmed quantitatively by the application of thermodynamic data to liquid phase thermal diffusion data. Future work is planned in this area.

ACKNOWLEDGMENT

The author would like to express his appreciation to Dr. R. Haase, Institut für physikalische Chemie, Aachen, Germany, for suggesting this additional work on the methane-*n*-butane system.

NOTATION

D_{12} = ordinary diffusion coefficient
h_i = partial specific enthalpy of component i
h_{i0} = specific enthalpy of component i in the dilute gas state
H_i = partial molar enthalpy of component i
J_i = mass flux of component i
k = Boltzmann constant
M_i = molecular weight of component i
$\overline{M}$ = average molecular weight, $x_1M_1 + x_2M_2$
p = pressure
q_1^* = heat of transport (heat transported per unit mass of moving molecules, including the enthalpy transport)
Q_1^{**} = heat of transport (heat transported per mole of moving molecules, less the enthalpy transport)
R = gas constant
T = temperature
x_i = mole fraction of component i

Greek Letters

α = thermal diffusion factor
α_0 = thermal diffusion factor for the dilute gas
ϵ = maximum attractive energy between two molecules
ρ = density
μ_i = chemical potential of component i
σ = collision diameter

LITERATURE CITED

1. De Groot, S. R., "Thermodynamics of Irreversible Processes," Interscience, New York (1951).
2. Denbigh, K. G., "The Thermodynamics of the Steady State," Wiley, New York (1951).
3. Prigogine, I., Thesis, L'Universite Libre de Bruxelles, Brussels (1947).
4. Rutherford, W. M., and J. G. Roof, *J. Phys. Chem.*, **63**, 1506 (1959).
5. Haase, R., *Z. Physik*, **127**, 1 (1950).
6. ———, *Z. Physik. Chem.*, **196**, 219 (1950).
7. Becker, E. W., and A. Schulzeff, *Naturwiss.*, **35**, 219 (1948).
8. Becker, E. W., *Z. Naturforschg.*, **5a**, 457 (1950).
9. Robb, W. L., and H. G. Drickamer, *J. Chem. Phys.*, **18**, 1380 (1950).
10. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
11. Benedict, M., G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **10**, 747 (1942).

Manuscript received March 6, 1963; revision received June 14, 1963; paper accepted June 27, 1963. Paper presented at A.I.Ch.E. Buffalo meeting.