Thermal Effects in Gas Absorption

The transformation of the energy equation from the mass average to the volume average reference frame exposes a pseudo Dufour effect. The theoretical model for absorption into a stagnant liquid including this effect, the heat of absorption, variable density, an interfacial velocity, and an arbitrary equilibrium condition at the interface is able to predict experimental data over a wide range of conditions. The data consisted of liquid temperature profiles and mass transfer rates into a stagnant liquid. The ammonia-water system exhibited interfacial temperature rises from 6.9°K to 18.2°K. The interfacial temperature rise for the propane-decane system was 1.3°K. Simpler theoretical models were able to predict the mass transfer rates or the temperature profiles.

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SCOPE

The objective of this study was to determine the extent to which theoretical calculations can predict gas absorption rates and liquid temperature profiles in unreactive gas absorption systems. Reactive systems in which the reaction is completed in the vicinity of the interface are naturally included.

Nonisothermal effects must be understood for the accurate design of industrial absorbers (Bourne et al., 1974). Temperature profiles are developed in the liquid solvent because of the energy released at the interface by the dissolving gas. The rise in surface temperature has been estimated as proportional to the heat of absorption in both binary (Danckwerts, 1953) and multicomponent systems (DeLancey, 1972). The surface temperature lowers the equilibrium concentration at the interface. A decrease in the mass transfer rate results. However, the extent of the reduction in the mass transfer rate may be reduced by volume changes in the liquid phase (Chiang and Toor, 1964).

The experimental aspect of this study is devoted to the simultaneous measurement of interfacial mass transfer rates and liquid temperature profiles over a range of physical conditions within which most gas absorption systems may be expected to fall. The ammonia-water system was studied at 1.00, 0.733, 0.467, and 0.200 atm. The propane-decane system was studied at 1.0 atm. Limited data are currently available for these systems as well as the butane-decane system (Chiang and Toor, 1964; Green and Chiang, 1971). The experiments were performed with a quiescent liquid phase. The surface renewal theory (Danckwerts, 1951) provides a vehicle for extending the results to the hydrodynamic conditions that are normally encountered in industrial absorbers.

A general theoretical development is included.

CONCLUSIONS AND SIGNIFICANCE

The assumption of constant density in liquid systems is generally inferior to the assumption of constant partial specific volumes. The latter assumption implies that the gas-liquid interface moves with the volume average velocity and that this velocity depends only on time. A coordinate system fixed to the interface then gives rise to a convective velocity in the liquid phase that is independent of the spatial coordinate. Attention is focused on an unreactive, unidirectional system.

In order to utilize the simplification of a uniform velocity, it is necessary to transform the usual form of the energy equation from the mass average frame to the volume average frame. The transformation exposes a conductive energy flow which is proportional to the concentration gradient in addition to the flow which is proportional to the temperature gradient. The former flow is referred to here as the pseudo Dufour effect.

An analytical solution of the simultaneous mass and energy balance equations in the volume average reference frame is obtained. The model applies to a semi-infinite liquid medium and includes the following effects:

1. Heat of absorption
2. Variable density
3. Arbitrary equilibrium condition at the interface
4. Pseudo-Dufour effect
5. Volume changes in the liquid phase.

The results are presented for binary systems. Results for multicomponent systems with thermodynamically coupled fluxes and solvent evaporation are available elsewhere (Verma, 1974).

The model is able to predict interfacial mass flows and temperature profiles in the liquid phase over a wide range of nonisothermal conditions. Comparisons of the model with the data from the ammonia-water systems spanned temperature rises from 6.9°K to 18.2°K. The propane-decane system exhibited a surface temperature rise of 1.3°K.

In all cases, the complete model was required to adequately predict the temperature profiles in the liquid phase and the interfacial mass transfer rates simultaneously.

If only the temperature profiles are desired, the pseudo Dufour effect may be neglected and a constant density assumed.

The interfacial mass transfer rate alone may be predicted with reasonable accuracy by assuming isothermal conditions, no interfacial velocity, and a constant density.

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Nonisothermal phenomena are present to some extent in all gas absorption operations. The importance of the nonisothermal effects arises from their influence on the mass transfer rate and, in the case of chemical absorption, from their influence on reaction rates and selectivities. The theoretical and experimental work presented here is limited to physical absorption.

The necessity of accounting for the energy transfer process has been demonstrated experimentally for a variety of cases. For example, Modine et al. (1963) have analyzed binary vaporization data in a wetted wall column for methanol and benzene into nitrogen and helium. Bourne et al. (1974) have studied the absorption of ammonia from air into water in a tray tower. In both studies, variations in temperature considerably affected the mass transfer process.

In many cases, the influence of temperature on the absorption process is estimated a priori by theoretical calculations (Danckwerts, 1970). These calculations are appropriately accomplished with the unsteady state penetration theory (Danckwerts, 1951) which can be directly incorporated into the time scale of processes in absorption equipment. However, the nonisothermal aspects of the model have scarcely been tested experimentally.

Chiang and Toor (1964) have demonstrated that the measurements of interfacial mass transfer rates may not, in all cases, reflect the presence of substantial temperature gradients in the liquid phase because of the opposition between the heat and volume change effects. Consequently, the question as to the adequacy of theoretical calculations for predicting temperature variations can only be answered by individual measurements of temperature profiles and mass transfer rates.

A knowledge of the nonisothermal behavior of the liquid is not only of importance in physical absorption. In chemical absorption, the local temperatures can substantially affect reaction rate and selectivity calculations. These calculations are often performed with the appropriate extension of theoretical models for physical absorption (Danckwerts, 1970). Consequently, it is important that the virtues of absorption theory with respect to the prediction of local temperatures be thoroughly ascertained in the unreactive case.

Green and Chiang (1971) have measured the temperatures in the vicinity of the interface in the butane-decane systems. Theoretical predictions of interfacial temperature rises of approximately 1.5°K and 7.5°K, respectively, were verified. A modification of their experimental technique was utilized here to measure interfacial mass transfer rates and temperature profiles in the liquid phase for the ammonia-water system and the propane-decane system. By varying the pressure of ammonia in the gas phase from 1.0 to 0.2 atm, interfacial temperature increases from approximately 18.2°K to 6.9°K were observed. Including the interfacial temperature rises for the propane-decane system, 1.3°K, a range of thermal effects within which most gas-absorption systems may be expected to fall has been studied. The experimental data are shown to be consistent with a new theoretical model of the absorption process. Simpler theoretical models are only partially consistent with the data.

REPRESENTATION OF ENERGY TRANSFER

In order to model the nonisothermal absorption process, it is necessary to consider the mass and energy balance equations simultaneously. From the viewpoint of the surface renewal theory (Danckwerts, 1951), the momentum transfer equation need not be included. However, volume changes in the liquid phase give rise to an interfacial velocity (Chiang and Toor, 1964). Consequently, the convective transport terms in the mass and energy balances must be retained and cast in the same frame of reference for simultaneous solution of the equations.

Energy transfer is naturally expressed in the mass average frame. In a unidirectional system, the mass average velocity is spatially uniform when the density is constant. In this case the mass balances may be easily written in the mass average frame (Toor, 1962) and the usual frame for the energy balance may be retained.

However, the assumption of constant density is generally inferior to the assumption of constant partial specific volumes. When the partial volumes are assumed to be constant, as will be done here, the volume average velocity is spatially uniform in a unidirectional, unreactive system. In this case the energy equation must be transformed from the mass average to the volume average frame in order to effectively utilize the simpler representation of convection.

Neglecting kinetic and potential energies, and work against viscous forces, the total energy flux may be written as

$$J_e = \rho u v^M + p v^M + q^M \tag{1}$$

or

$$J_e = \sum_{i=1}^{N} \hat{H}_i J_i + q \tag{2}$$

for a unidirectional system. The energy flux q is seen to be independent of the reference frame and is given by

$$q = q^M - \sum_{i=1}^{N} \hat{H}_i j_i^M \tag{3}$$

Assuming that the pressure, partial specific enthalpies, specific heat of the mixture, and the partial specific volumes are constant, the energy equation for a unidirectional system may be written as (Verma, 1974)

$$\frac{\partial(\rho c_p T)}{\partial t} + \frac{\partial}{\partial x}(q + \rho c_p T v^M) = 0 \tag{4}$$

Gravity is taken as the only external force and chemical reactions are not considered. Note that the density has not been assumed to be constant.

If the velocity is transformed to the volume average frame (Verma, 1974), Equation (4) becomes

$$\frac{\partial(\rho c_p T)}{\partial t} + \frac{\partial}{\partial x}(q^V + \rho c_p T v^V) = 0 \tag{5}$$

where

$$q^V = q + c_p T \sum_{i=1}^{N} \left(1 - \frac{\hat{V}_i}{\hat{V}_N}\right) j_i^V \tag{6}$$

If thermodynamic coupling is ignored, that is,

$$q = -k \frac{\partial T}{\partial x} \tag{7}$$

and

$$j_i^V = -D_{im}^V \frac{\partial \rho_i}{\partial x} \tag{8}$$

then Equation (6) may be written as

$$q^V = -\sum_{i=1}^{N} c_p T \left(1 - \frac{\hat{V}_i}{\hat{V}_N}\right)(D_{im}^V - \alpha)\frac{\partial \rho_i}{\partial x} - \alpha \frac{\partial(\rho c_p T)}{\partial x} \tag{9}$$

after the substitutions implied by Equations (7) and (8). The energy flux q^V is seen to depend upon the gradients in concentration in a way that is similar to the Dufour effect, although this phenomenon is not considered here (DeLancey and Chiang, 1968). The relationship between q^V and $\partial \rho_i / \partial x$ in Equation (9) will be referred to here as the pseudo Dufour effect.

The expression of q^V that results from the postulates of irreversible thermodynamics are available elsewhere (Verma, 1974), as well as the continuation of the development for multicomponent systems. The development here will proceed for binary systems.

THEORETICAL MODEL

The mass and energy balances may now be summarized for a binary liquid phase as

$$\frac{\partial \rho_A}{\partial t} + v^V \frac{\partial \rho_A}{\partial x} = D_{AB}{}^V \frac{\partial^2 \rho_A}{\partial x^2} \tag{10}$$

and

$$\frac{\partial \rho_e}{\partial t} + v^V \frac{\partial \rho_e}{\partial x} = D_{qA}{}^V \frac{\partial^2 \rho_A}{\partial x^2} + \alpha \frac{\partial^2 \rho_e}{\partial x^2} \tag{11}$$

where

$$D_{qA}{}^V = \rho c_p T \left(1 - \frac{\hat{V}_A}{\hat{V}_B}\right)(D_{AB}{}^V - \alpha) \tag{12}$$

and

$$\rho_e = \rho c_p T \tag{13}$$

The transport coefficients $D_{qA}{}^V$, α, and $D_{AB}{}^V$ will be assumed constant. The temperature in Equation (12) will be set at the average of the bulk and surface values.

For a quiescent liquid (B), that is suddenly contacted with a gas containing the soluble component (A), the boundary and initial conditions may be set as follows:

1. Uniform initial conditions:

$$\rho_i(x, 0) = \rho_i{}^\infty, \quad i = A, e; \quad x > 0 \tag{14}$$

2. Semi-infinite liquid:

$$\rho_i(\infty, t) = \rho_i{}^\infty, \quad i = A, e; \quad t > 0 \tag{15}$$

The assumption of an infinite liquid medium in the direction of mass transfer is valid for sufficiently short contact times.

3. Equilibrium at the interface:

$$\rho_A(0, t) = a\,\rho_e(0, t) + b \quad t \geqq 0 \tag{16}$$

It is not necessary that the equilibrium relation be linear. The method of solution is to preset the interfacial values of ρ_A and ρ_e. They may then be related by any functional form as a final step in the solution. If the solution is unique, the functional form may be considered specified at the outset, which does not require that the surface values be constant.

As the value of a is generally negative, an increase in the surface temperature has a deleterious affect on the mass transfer process by lowering the value of the surface concentration. Estimates of rises in the surface temperature have been reported to be proportional to the heat of absorption for both binary (Danckwerts, 1953) and multicomponent systems (DeLancey, 1972).

4. Energy transfer:

Assuming that the solvent is nonvolatile, and that there is no sensible energy transfer between the gas and liquid phases, an interfacial energy balance results in

$$q^V = -\left[\frac{H_A}{1 - \rho_A \hat{V}_A} + c_p T\left(1 - \frac{\hat{V}_A}{\hat{V}_B}\right)\right] D_{AB}{}^V \frac{\partial \rho_A}{\partial x}, \quad x = 0 \tag{17}$$

If free convection of energy at the interface were considered, a variation in the surface temperature with time may result (Green and Chiang, 1971). Such a result will not be needed here to represent the experimental data. Also, if the solvent were considered to be volatile, a cooling effect would result at the interface which would offset, to some degree, the deleterious effect of an exothermic absorption process. In the experimental apparatus, which is described below, the solvent will evaporate until the gas space above the liquid becomes saturated. Approximate calculations of the required evaporation rate relative to the gas absorption rate and the agreement of the proposed model with the experimental data indicate that solvent evaporation is not an important consideration in the experiments reported here. Solvent evaporation is considered in the more general result reported elsewhere (Verma, 1974).

The solution to the problem thus stated may be obtained using the combination variable, $y = x/(2\sqrt{t})$. The resulting interfacial conditions are given by

$$J_A(0, t) = \frac{\rho_A{}^0 - \rho_A{}^\infty}{1 - \rho_A{}^0 \hat{V}_A} \sqrt{\frac{D_{AB}{}^V}{\pi t}} \frac{e^{-\lambda^2/D_{AB}{}^V}}{1 + \operatorname{erf}(\lambda/\sqrt{D_{AB}{}^V})} \tag{18}$$

where

$$v^V = \lambda/\sqrt{t} \tag{19}$$

$$\lambda = \frac{\hat{V}_A}{\rho_A{}^0 \hat{V}_A}(\rho_A{}^0 - \rho_A{}^\infty) \sqrt{\frac{D_{AB}{}^V}{\pi}} \frac{e^{-\lambda^2/D_{AB}{}^V}}{1 + \operatorname{erf}(\lambda/\sqrt{D_{AB}{}^V})} \tag{20}$$

$$\frac{\rho_e{}^0 - \rho_e{}^\infty}{\rho_A{}^* - \rho_A{}^\infty} = \frac{\dfrac{H_A}{1 - \rho_A{}^0 \hat{V}_A} \dfrac{\sqrt{D_{AB}{}^V}\, e^{-\lambda^2/D_{AB}{}^V}}{1 + \operatorname{erf}(\lambda/\sqrt{D_{AB}{}^V})} + c_p T\left(1 - \dfrac{\hat{V}_A}{\hat{V}_B}\right) \dfrac{\sqrt{\alpha}\, e^{-\lambda^2/\alpha}}{1 + \operatorname{erf}(\lambda/\sqrt{\alpha})}}{\dfrac{H_A}{1 - \rho_A{}^0 \hat{V}_A} \dfrac{\sqrt{D_{AB}{}^V}\, e^{-\lambda^2/D_{AB}{}^V}}{1 + \operatorname{erf}(\lambda/\sqrt{D_{AB}{}^V})} + \dfrac{\sqrt{\alpha}\, e^{-\lambda^2/\alpha}}{1 + \operatorname{erf}(\lambda/\sqrt{\alpha})}} \tag{21}$$

$$\rho_A{}^0 = a\,\rho_e{}^0 + b \tag{22}$$

$$\rho_A{}^* = a\,\rho_e{}^\infty + b \tag{23}$$

The temperature profiles in the liquid phase are given by

$$\begin{aligned} \rho_e{}^0 - \rho_e = {} & (\rho_e{}^0 - \rho_e{}^\infty) \frac{\operatorname{erf}\left(\dfrac{y - \lambda}{\alpha}\right) + \operatorname{erf}\left(\dfrac{\lambda}{\sqrt{\alpha}}\right)}{1 + \operatorname{erf}(\lambda/\sqrt{\alpha})} \\ & + c_p T\left(1 - \frac{\hat{V}_A}{\hat{V}_B}\right)(\rho_A{}^0 - \rho_A{}^\infty) \\ & \left[\frac{\operatorname{erf}\left(\dfrac{y - \lambda}{\sqrt{D_{AB}{}^V}}\right) + \operatorname{erf}\left(\dfrac{\lambda}{\sqrt{D_{AB}{}^V}}\right)}{1 + \operatorname{erf}(\lambda/\sqrt{D_{AB}{}^V})} \right. \\ & \left. - \frac{\operatorname{erf}\left(\dfrac{y - \lambda}{\sqrt{\alpha}}\right) + \operatorname{erf}\left(\dfrac{\lambda}{\sqrt{\alpha}}\right)}{1 + \operatorname{erf}(\lambda/\sqrt{\alpha})}\right] \end{aligned} \tag{24}$$

The interfacial conditions and temperature profiles in the liquid phase have been evaluated for the systems that were studied experimentally.

CALCULATIONS

In order to calculate the interfacial velocity and surface temperature, a trial and error procedure was followed. A value of ρ_e^0 was assumed and used to calculate λ with Equation (20). A new value of ρ_e^0 was then calculated with Equation (21). The new value of ρ_e^0 was then used to recalculate λ. The process was repeated until the difference between successive values of ρ_e^0 was less than unity. In each trial, the values of a and b in Equation (22) were adjusted to match the current slope in the equilibrium data. The diffusivity D_{AB}^V was also evaluated at the current surface temperature. Consequently, the final values of a, b, and D_{AB}^V correspond to the resulting surface conditions. A more detailed discussion of the calculation procedure is given in the Supplement.[*]

Calculations have been carried out for the propane-decane system and the ammonia-water system at four different pressures. The gas phase is considered to consist only of the absorbing species. The preset parameters used in the calculations are listed in Table 1.

The value of the liquid phase diffusivity in the ammonia (A)-water (B) system at 298°K (Perry, 1973) was corrected to other temperatures in the range of interest by assuming that $D_{AB}^V/(\mu T)$ is constant:

$$D_{AB}^V = \frac{6.90 \times 10^{-12}\, T}{0.8937 - 0.0158\,(T - 298)} \quad (\mathrm{m^2/s}) \qquad (25)$$

The diffusivity in the propane (A)-decane (B) system was taken from Green (1968):

$$D_{AB}^V = 7.804 \times 10^{-8}\, e^{-865/T} \quad (\mathrm{m^2/s}) \qquad (26)$$

Equilibrium data for the ammonia-water system have been reported by Clifford and Hunter (1933). For each pressure, the equilibrium mole fraction of ammonia is linearly related to temperature over the range of interest:

$$x_A = a_1\,(T - 273.2) + b_1 \qquad (27)$$

The values of a_1 and b_1 are listed in Table 2. The values of a_1 and b_1 for the propane-decane system were obtained from Reamer and Sage (1964).

The density of each system was evaluated with

$$\rho = \rho_A \left(1 - \frac{\hat{V}_A}{\hat{V}_B}\right) + \frac{1}{\hat{V}_B} \qquad (28)$$

The calculated surface conditions are given in Table 3. The calculated temperature profiles will be reported with the measured values.

EXPERIMENT

The experimental apparatus is illustrated in Figure 1. The absorption cell is a pyrex cylindrical vessel (diameter = 0.149 m, height = 0.203 m) fitted with a gasket and a stainless steel cover. All instrumentation and service lines are connected to the steel plate which is screwed to the glass cell. The cell is partially insulated. A window is provided in the insulation to view the gas-liquid interface.

The solvent liquid is introduced under vacuum into the cell through a fill wand. The liquid is thoroughly degassed before an absorption run is begun. Consequently, the initial pressure in the cell is the vapor pressure of the solvent at the ambient temperature.

A chromel-constantan thermocouple with a tip thickness of 5.08 μm is positioned in the liquid by means of a machine screw through the cover plate. The penetration of the interface by the thermocouple is determined visually. The thermocouple

TABLE 1. PREFIXED MODEL PARAMETERS

Parameter	NH_3 (A)-H_2O (B)	C_3H_8 (A)-$C_{10}H_{22}$ (B)
$\hat{V}_A$ (m³/kg)	1.471×10^{-3}[a]	1.791×10^{-3}[d]
$\hat{V}_B$ (m³/kg)	1.003×10^{-3}[b]	1.368×10^{-3}[d]
c_p (kJ/kg · °K)	4.18[b]	2.22[e]
α (m²/s)	1.416×10^{-7}[b]	9.084×10^{-8}[f]
H_A (MJ/kg)	1.875[c]	0.502[g]
T^∞ (°K)	297.5	297.5
$\rho_A{}^\infty$ (kg/m³)	0.0	0.0
ρ^∞	997	731

[a] Chiang and Toor (1964).
[b] Perry (1973).
[c] Hougen, et al. (1968).
[d] Graue and Sage (1967).
[e] Timmermans (1965).
[f] Carmichael et al. (1968).
[g] Budenholzer et al. (1943).

TABLE 2. EQUILIBRIUM DATA

System	P(atm)	$-a_1 \times 10^3$(°K)$^{-1}$	b_1
NH_3-H_2O	1.000	5.75	0.477
NH_3-H_2O	0.733	5.45	0.424
NH_3-H_2O	0.467	5.12	0.360
NH_3-H_2O	0.200	4.30	0.245
C_3H_8-$C_{10}H_{22}$	1.000	3.68	0.195

TABLE 3. CALCULATED MASS TRANSFER AND SURFACE PARAMETERS

System	p (atm)	$-a \times 10^7$ (kg/J)	b (kg/m³)	$D^V{}_{AB} \times 10^9$ (m²/s)	K × 10²[*] (kg/m² · ½)	$\lambda \times 10^5$ (m/s½)	ΔT_s (°K)	ρ° (kg/m³)
NH_3 (A)-H_2O (B)	1.000	1.76	412	3.63	1.561	1.148	18.2	902
NH_3 (A)-H_2O (B)	0.733	1.60	370	3.30	1.295	0.953	14.9	913
NH_3 (A)-H_2O (B)	0.467	1.38	318	3.02	1.030	0.758	11.7	926
NH_3 (A)-H_2O (B)	0.200	0.995	221	2.62	0.620	0.456	6.9	950
C_3H_8 (A)-$C_{10}H_{22}$ (B)	1.000	0.466	47	4.28	0.186	0.167	1.3	723

[*] $K = \dfrac{1}{2\sqrt{t}} \displaystyle\int_0^t J_A(0, \tau)\, d\tau$

$Q = 2K\sqrt{t}$

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[*] The Supplement has been deposited as Document No. 02523 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 40 Park Ave S., N. Y., N. Y. 10016 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

was bent to a right angle near its tip to aid in the determination of the penetration point and to keep the hot junction in an isothermal plane. The emf output of the thermocouple is continuously recorded.

The gas to be absorbed is introduced to the space above the liquid in the cell. The inlet gas impinges upon a baffle plate located in the gas space to eliminate disturbance of the gas-liquid interface. A solenoid valve is used to initially introduce the gas into the cell. The time required for the cell to reach the desired pressure was negligible.

The gas supply for the cell is located upstream. The gas is supplied to the cell at the rate required to maintain a constant cell pressure. The flow of gas to the cell is automatically regulated by a pressure control valve when the absorption rate is moderate. At high absorption rates, the gas flow is regulated manually with a needle valve or a fine metering valve, according to a visual observation of the pressure in the cell. The three valves are located in a three pronged manifold prior to the absorption cell.

The upstream gas pressure is monitored automatically by a pressure transducer. The constant volume upstream of the pressure control valves was experimentally determined and verified by numerical calculations. Consequently, the rate of decrease of the upstream pressure is proportional to absorption rates. The gas storage may be rapidly replenished, if necessary, during an absorption run through the use of several solenoid valves. The output of the pressure transducer as well as the thermocouple output, are continuously recorded on a two-pen recorder.

EXPERIMENTAL RESULTS

The propane-decane system was studied at 1.0-atm pressure of pure propane over decane. The measured temperature profile is shown in Figure 2. The cumulative mass transfer, per unit area of the gas-liquid interface, is shown in Figure 3.

The temperature profile was obtained by making eight runs under the same experimental conditions, save for the initial position of the thermocouple. Because of the movement of the interface, the position of the thermocouple advanced deeper into the liquid phase as the experiment proceeded. The depth of the thermocouple below the interface (x) was determined with the calculated value of λ as

$$x = x^0 + 2\lambda\sqrt{t} \tag{29}$$

The initial depth is denoted by x^0. The value of y was then computed

$$y = \frac{x^0}{2\sqrt{t}} + \lambda \tag{30}$$

The initial positions of the thermocouple are given in Table 4.

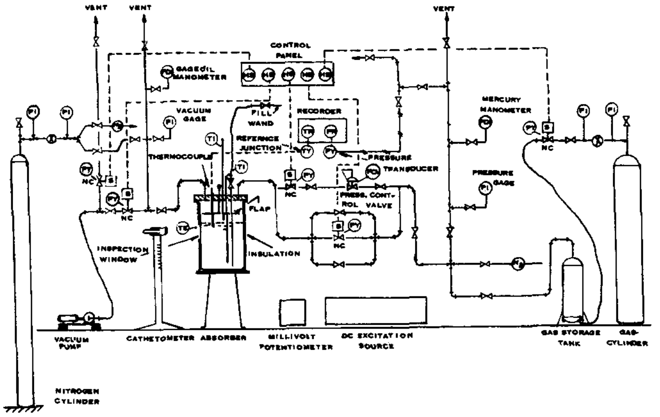

Fig. 1. Experimental apparatus.

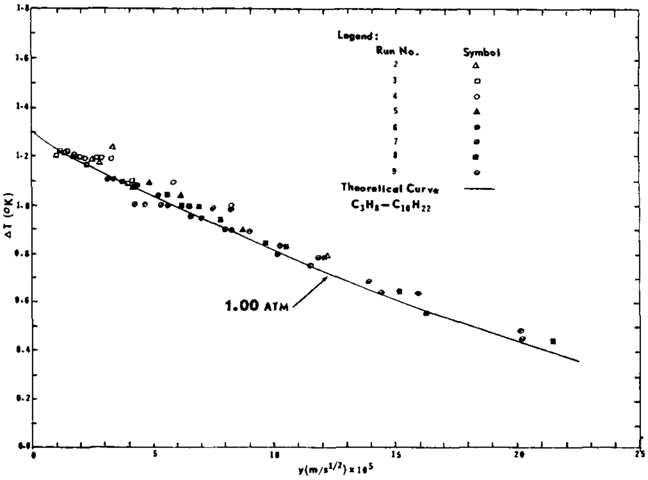

Fig. 2. Temperature profile in propane-decane system.

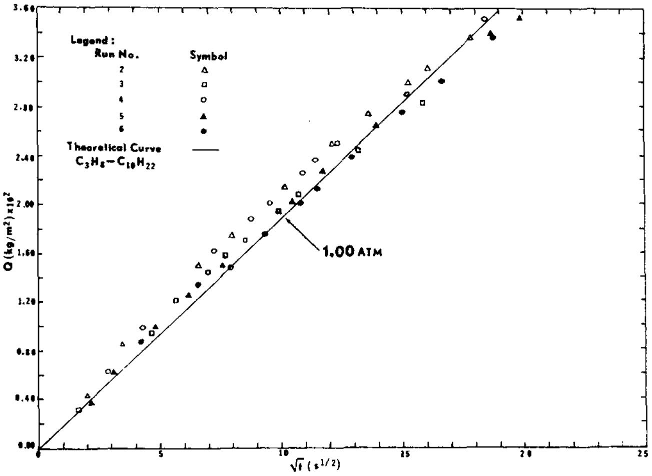

Fig. 3. Cumulative mass transfer in propane-decane system.

TABLE 4. INITIAL THERMOCOUPLE POSITIONS (μm)

Run no.	x^0 for C_3H_8-$C_{10}H_{22}$ system	x^0 for NH_3-H_2O system $p = 1.0$ atm	$p = 0.733$ atm	$p = 0.467$ atm	$p = 0.200$ atm
2	0+	—	0+	0+	2.54
3	2.54	5.08	—	—	7.62
4	5.08	7.62	5.08	2.54	—
5	7.62	10.2	7.62	5.08	—
6	10.2	12.7	10.2	—	12.7
7	12.7	19.1	12.7	7.62	19.1
8	19.1	0+	19.1	10.2	—
9	25.4	2.54	2.54	12.7	—
10	—	—	—	19.1	—

Several measurements of the initial and final positions of the interface were taken. These values broadly supported the use of the calculated value of λ. Experimental limitations precluded the measurement of λ.

The absorption rate data were determined from the transient pressure measurements in the known volume upstream of the absorption cell. The upstream pressure gradually decreased as the gas in the constant pressure absorption cell was replenished. Ideal behavior was assumed for the calculations.

Similar measurements were made for the ammonia-water system at four different pressures of ammonia: 1.0, 0.733, 0.467, and 0.20 atm. The temperature profiles are presented in Figures 4 and 5. The absorption rate data are presented in Figures 6 and 7.

ANALYSIS OF RESULTS

The theoretical results presented earlier are indicated in the graphical representation of the experimental results. In each case, the theoretical curve is seen to be in reasonable agreement with the measured values. It should be noted that no effort was expended to obtain the best match between the theoretical and experimental results. Such a search could be made by determining the optimum conditions between the bulk and surface of the liquid at which the model parameters should be evaluated.

If the pseudo-Dufour effect (PDE) is neglected, the comparison between the calculated and experimental results deteriorates. For example, considering the ammonia-water system at 1.0 atm, the prediction of the interfacial flux would be 23.0% less than the value computed with the PDE included. The predicted surface temperature rise increases to 48.3°K.

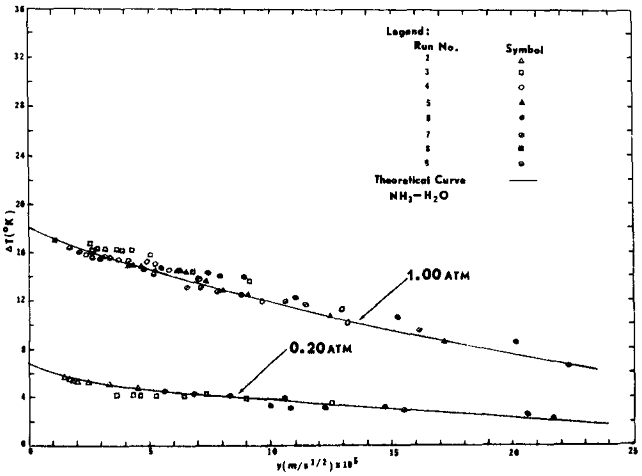

Fig. 4. Temperature profiles in ammonia-water system.

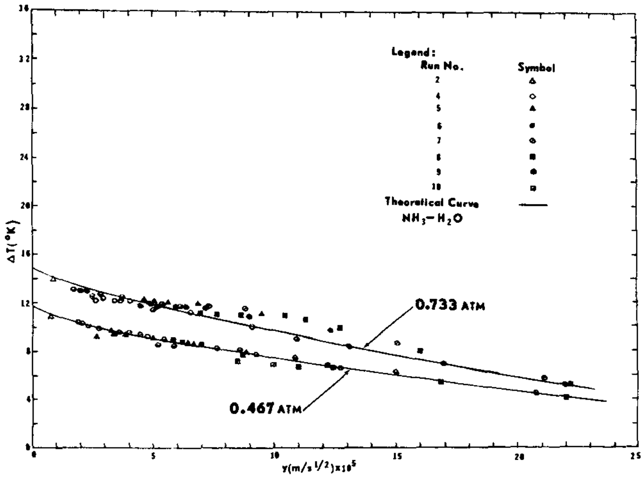

Fig. 5. Temperature profiles in ammonia-water system.

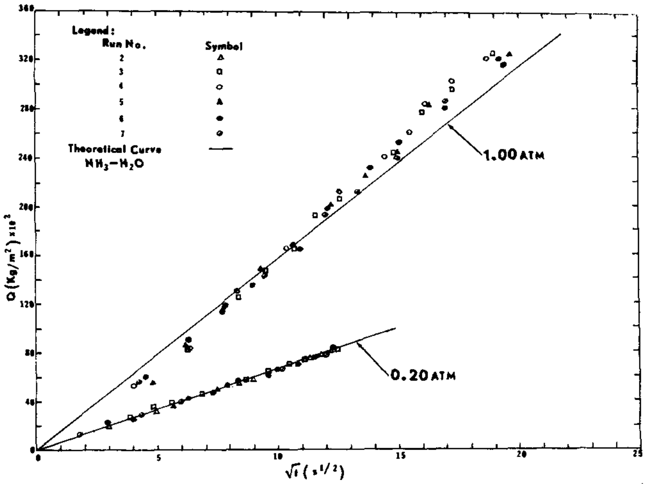

Fig. 6. Cumulative mass transfer in ammonia-water system.

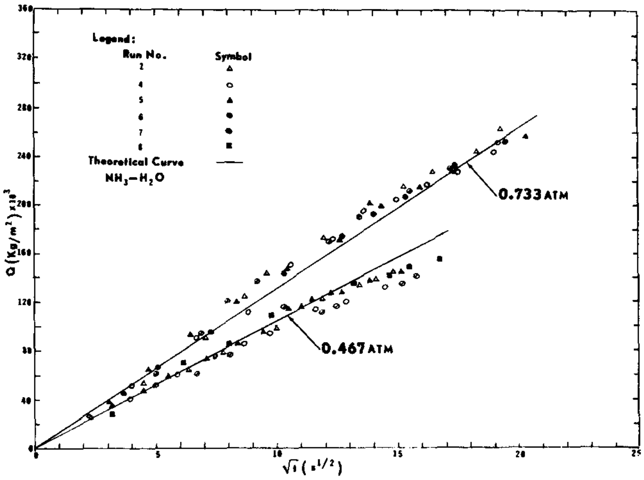

Fig. 7. Cumulative mass transfer in ammonia-water system.

If the density variations are also neglected, the prediction of the interfacial flux is 11.5% less than the value without the additional assumptions. The effect on the temperature profile is not as severe, being within 3.8% of the value calculated with a variable density and the PDE.

If the PDE is included but variations in the density are neglected, the maximum temperature occurs beneath the liquid surface (Verma, 1974). A maximum value of 1.29 GJ/m^3 for ρ_e occurs at $y = 0.01$. On this basis, a temperature wave would travel through the liquid phase at the velocity of the interface. This was not observed in the experiments.

If the movement of the interface is neglected and a constant density is assumed (DeLancey, 1972), the prediction of the interfacial temperature rise decreases by 16.6%. The interfacial mass flux decreases by 8.1%. If, in addition, the interfacial temperature rise is ignored, the interfacial mass flux is 3.6% less than the value calculated with the complete model.

These comparisons are summarized in Table 5. Additional comparisons are also available (Verma, 1974). In making the calculations, the equilibrium and diffusivity data used with Model I were employed. When density

Table 5. Comparison of Calculated Interfacial Temperature and Mass Flux in Ammonia Water System at 1.0 atm

Model	Pseudo Dufour effect	Surface temperature rise	Variable density	Interfacial velocity	ΔT_s (°K)	$K \times 10^2$ (kg/m$^2 \cdot$ s$^{1/2}$)
I	yes	yes	yes	yes	18.2	1.561
II	no	yes	yes	yes	48.3	1.188
III	no	yes	no	yes	17.5	1.384
IV	no	yes	no	no	15.2	1.435
V	no	no	no	no	0.0	1.505

was assumed to be constant, it was set at the bulk value.

The interfacial temperature rise reported here for the propane-decane system agrees with that presented by Green and Chiang (1971). The absorption rate data for the ammonia-water system at 1.0 atm, when extrapolated to very short contact times, agrees with the data presented by Chiang and Toor (1964) for contact times less than 0.02 s.

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NOTATION

a, a_1 = equilibrium parameter defined by Equations (16) and (27), respectively

b, b_1 = equilibrium parameter defined by Equations (16) and (27), respectively

c_p = specific heat of mixture

D_{im} = diffusion coefficient for species i in mixture

D_{AB} = diffusion coefficient for species A in binary mixture of A and B

D_{qA} = coefficient for pseudo Dufour energy flux

$\hat{H}_i$ = partial specific enthalpy of species i

H_A = energy released by species A upon absorption

J_e = total energy flux

J_A = total flux of species A

j_i = diffusional flow of species i

k = thermal conductivity of mixture

K = interfacial flux parameter (see Table 3)

N = number of components in multicomponent mixture

p = pressure

Q = net interfacial mass transfer

q = diffusional energy flux

T = absolute temperature

t = time

u = internal energy of mixture

v = velocity

$\hat{V}_i$ = partial specific volume of species i

x = distance into liquid phase from gas-liquid interface

y = combined variable $(= x/2\sqrt{t})$

Greek Letters

α = thermal diffusivity of mixture

ΔT_s = interfacial temperature rise above bulk value

λ = velocity parameter

ρ = density of liquid mixture

ρ_i = concentration of species i

ρ_e = scaled temperature variable defined by Equation (13)

Superscripts

∞ = at distances far from the gas-liquid interface

o = at the gas-liquid interface

M = mass average velocity frame

V = volume average velocity frame

$*$ = equilibrium corresponding to bulk liquid temperatures

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