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THE UNIVERSITY OF ALBERTA

ISOTOPIC EXCHANGE OF DEUTERIUM IN THE HYDROGEN-AMINOMETHANE SYSTEM

by

© JOHN M. MALCOLM

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "Isotopic Exchange of Deuterium in the Hydrogen-Aminomethane System" submitted by John M. Malcolm in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

A single sphere absorber was used to obtain measurements of the pseudo-first-order rate constant for the isotopic exchange of deuterium in the hydrogen-aminomethane system. The catalysts used in this study were potassium methylamide (PMA) and mixtures of potassium and lithium methylamides (PLMA). The temperature range of the investigation was -10 to -50°C and an activation energy of 28.5 kJ/mol was calculated for the reaction. Values of the rate constants ranged from 2.1 to 382 s^{-1}.

Two sets of experiments were performed with PMA catalyst concentrations of 0.31 and 0.40 m mol/g amine. These data along with data from Rochard (3) and Kalra and Otto (2) were used to develop a model of the dependence of the rate constant on PMA concentration.

Rate constants were measured for solutions containing lithium methylamide to potassium methylamide concentration ratios ranging from 0.5 to 4.26. An equation was developed, using all the data obtained in this work, which describes the dependence of the rate constant on temperature, PMA concentration and lithium methylamide concentration.

The accuracy of the rate constants obtained was estimated to be ± 10%.

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1. INTRODUCTION

The exchange of deuterium between hydrogen and aminomethane has potential to form the basis for a process for the commercial production of heavy water, that would provide an alternative to the H_2O-H_2S exchange process now used in Canada. Bancroft and Rae (1) have described a bithermal hydrogen-aminomethane exchange process that would operate between the temperatures of -40°C and 70°C. The feedstock would consist of a large source of hydrogen or alternatively water could be used as a feed by providing a hydrogen-water exchange step. Possible large sources of hydrogen are the synthesis gas feeds to large scale fertilizer or ammonia plants and the hydrogen which may be produced for use in the upgrading of the bitumen from the oil sands.

The naturally occurring ratio of deuterium to hydrogen is in the order of $1.5 \times 10^{-4}:1$. Thus large quantities of feed must be processed to produce a significant quantity of D_2O (in the first enrichment stage) and very large liquid-gas contactors are required. These contactors constitute a major portion of the capital cost of a heavy water plant.

The hydrogen-aminomethane exchange shown as

$$CH_3NH_2 + HD \rightleftarrows CH_3NHD + H_2 \qquad (1.1)$$

is a fast reaction which occurs in the liquid phase and is catalyzed by alkali metal amides dissolved in the amine. Quantitative information on the effects of temperature and amide concentration on the rate of exchange is useful for the estimation of transfer coefficients and thus stage efficiencies for the design of industrial gas-liquid contactors.

Published kinetic data for the hydrogen-aminomethane exchange are limited to that of Kalra and Otto (2), Rochard (3) and Bar-Eli and Klein (4). Bar-Eli and Klein observed that the rate of exchange in the hydrogen-aminomethane system was higher than that in the hydrogen-ammonia system. The measurements of Rochard and Bar-Eli and Klein were obtained with stirred reactprs and the resistance to mass transfer was not entirely eliminated or accounted for. Consequently the only reliable rate data from these investigations are those obtained by Rochard for very low temperatures and catalyst concentrations.

Kalra obtained rate data with aminomethane solutions containing catalyst concentrations of greater significance for the design of industrial contactors. However his investigation covered a fairly narrow temperature range and the reported value of the activation energy for the reaction, 14.9 kJ/mol, was much lower than the value reported by Rochard, 28.4 kJ/mol. An objective of this study was to obtain additional rate data for high potassium methylamide (PMA) concentrations and to investigate the discrepancy in the reported values of the activation energy.

The use of a mixture of lithium methylamide and potassium methylamide (PLMA) as a catalyst for the hydrogen-aminomethane exchange is reported to have several process advantages (5). An additional objective of this study was to investigate the effect of the addition of lithium methylamide as catalyst.

Kalra and Otto (2) demonstrated that the single sphere absorber is a convenient device for the measurement of the reaction rate constants for this fast exchange reaction. Consequently the sphere absorber was also selected for this study.

2. LITERATURE SURVEY

2.1 Hydrogen-Ammonia System

Exchange studies of the hydrogen-ammonia system are of interest in the study of the hydrogen-aminomethane system since aminomethane is a simple substituted derivative of ammonia. The hydrogen-ammonia reaction may be written as

$$NH_3 + HD \rightleftarrows NH_2D + H_2 \qquad (2.1)$$

Wilmarth and Dayton (6) used a stirred reactor to study the ortho-para conversion of hydrogen and the isotopic exchange of hydrogen with liquid ammonia. They determined that the above reaction, Equation (2.1), was homogeneous and that the rate was first order with respect to the concentration of dissolved hydrogen deuteride. Their data on the hydrogen exchange reaction consisted of two measurements at -53°C with very low potassium amide concentrations of 0.15 and 2.7 m mol/l. The rate constants obtained for these catalyst concentrations were 0.23 and 1.31 min^{-1}, respectively. A linear dependence of the rate constant on the catalyst concentration was observed from their data.

Bar-Eli and Klein (7) also used a stirred reactor to study the hydrogen-ammonia system using potassium, sodium and lithium amide catalysts. Their investigation covered the temperature range 0 to -80°C with catalyst concentrations from 5-200 m mol/l. An activation energy of 31.4 kJ/mol was calculated for the reaction with potassium amide as catalyst. The rate of exchange at -61°C with a saturated potassium amide solution was 5.5 times that obtained with a saturated sodium amide solution. Similarly, the ratio of the rate of exchange measured for a saturated solution of sodium amide to that for a saturated solution of lithium amide at -43°C was 23:1. The rate of reaction had a linear dependence on the catalyst concentration over the range studied. However, the positive intercept on the rate constant versus catalyst concentration curve at zero catalyst concentration plus the work of Wilmarth and Dayton (6) on the ortho-para conversion of hydrogen at high catalyst concentrations, led them to propose that the isotope exchange is catalyzed by both the free amide ion and the undissociated potassium amide. They expressed this relationship as

$$k = k_{NH_2^-} [NH_2^-] + k_{KNH_2} [KNH_2] \qquad (2.2)$$

where $k_{NH_2^-}$ and k_{KNH_2} are the specific rate constants for the catalysis by the amide ion and potassium amide, respectively.

Dirian et al. (8) studied the exchange reaction in the temperature range -70 to -40°C with catalyst concentrations from 0.4 to 1400 m mol/1. They were unable to eliminate the mass transfer resistance with catalyst concentrations greater than 60 m mol/1, in spite of stirrer speeds up to 9000 rpm. A value of 33.5 kJ/mole was reported for the activation energy of the reaction. They proposed that the dependence of the rate constant on the catalyst concentration should be expressed in terms of the activities of NH_2^- and KNH_2 as

$$k = k_{NH_2^-} a_{NH_2^-} + k_{KNH_2} a^2_{KNH_2} \qquad (2.3)$$

where $a_{NH_2^-}$ and a_{KNH_2} are the activities of the amide ion and the undissociated amide, respectively.

Delmas et al. (9) also used a stirred reactor to investigate the hydrogen-ammonia exchange reaction, with particular emphasis on determining the catalytic active specie. Their results, at -45.2°C, indicated a linear dependence of the rate constant on the concentration of potassium amide up to about 5 m mol/l. Above this concentration the observed rate was higher than that predicted by extrapolation of the linear region of the curve. They proposed that NH_2^- was the only catalytic active specie and the rate constant could be expressed as

$$k = k_o[NH_2^-] \quad , \qquad (2.4)$$

The increased rate observed at potassium amide concentrations greater than 5 m mol/l was thought to be due to an increase in the NH_2^- concentration, caused by the formation of triple ions of the form $K_2NH_2^+$. The activation energy calculated from their data between -45.2 and -70.0°C was 23.0 kJ/mol. They attributed the difference between this value and that determined by Bar-Eli and Klein (7) to the use of different values for the solubility of hydrogen.

Bourke and Lee (10) used both a wetted rod contactor and a disc column to study the exchange reaction with potassium amide as the catalyst. The flow of ammonia on the rod was laminar which allowed them to account for the liquid phase resistance to the transfer of HD. They investigated the temperature range -40 to +20°C with catalyst concentrations of 0.082, 0.163, 0.327 and 0.653 mol/l. The rate constants ranged from 10 to 500 s^{-1} and an activation energy of 33.5 kJ/mole was calculated.

2.2 Hydrogen-Aminomethane System

The isotopic exchange of deuterium in the hydrogen-aminomethane system may be written as

$$CH_3NH_2 + HD \rightleftarrows CH_3NHD + H_2 \qquad (1.1)$$

The system properties of particular interest in a kinetic study of this reaction are:

1. The solubility of hydrogen in aminomethane
2. The diffusivity of HD in aminomethane
3. The equilibrium constant for the reaction
4. The solubility of the alkali amides in aminomethane

Moore (11) measured the solubility of hydrogen in aminomethane over the temperature range -60 to +25°C with pressures up to 300 psig. He expressed the solubility in terms of the Henry's law coefficient as

$$\ln H = A_0 + A_1\beta + A_2\beta^2 \qquad (2.5)$$

where H = Henry's law coefficient (atm/mole fraction)

$A_0 = 4.1403$

$A_1 = 1.6612$

$A_2 = -0.1160$

$\beta = 10000.0/T$

Kalra (12) measured the diffusivity of hydrogen in liquid aminomethane in the temperature range -20 to -30°C. The use of a modified Ferrell and Himmelblau correlation shown as

$$D = 4.66 \times 10^{-7} \frac{T}{\mu_1^{\alpha_1}} \left[\frac{1 + \Lambda^{*2}}{V_2}\right]^{0.53} \qquad (2.6)$$

where D = Diffusivity (cm^2/s)

T = Temperature (K)

μ_1 = Viscosity of the solvent (cp)

α_1 = Property of the solute = $\sigma/[\frac{V_2}{N}]^{1/3}$

V_2 = Molar volume of the solute (cm^3/mol)

Λ^* = Quantum parameter = $h/\sigma(m\varepsilon)^{1/2}$

for the prediction of the diffusivities of H_2, HD and D_2 in aminomethane was recommended.

The gas phase equilibrium constant for the reaction, Equation (1.1), and the relative volatility of CH_3NH_2/CH_3NHD may be written as

$$K_{eq} = \frac{[CH_3NHD]_g[H_2]_g}{[CH_3NH_2]_g[HD]_g} \tag{2.7}$$

and

$$\alpha_N = \frac{[CH_3NH_2]_g[CH_3NHD]_\ell}{[CH_3NH_2]_\ell[CH_3NHD]_g} \tag{2.8}$$

The separation factor is defined as

$$\alpha = \frac{\text{D/H ratio in gas-free amine}}{\text{D/H ratio in vapor-free hydrogen}} \tag{2.9}$$

For the case of low deuterium concentration the separation factor may be expressed in terms of the gas phase equilibrium constant and the relative volatility as

$$\alpha = K_{eq}\,\alpha_N\,\frac{n^*}{m^*} \tag{2.10}$$

where n^* = Number of exchangeable hydrogen atoms in an aminomethane molecule

m^* = Number of exchangeable hydrogen atoms in a hydrogen molecule

The number of exchangeable hydrogen atoms in both an aminomethane and a hydrogen molecule is two, which indicates that the term $n^*/m^* = 1$ for this system, thus

$$\alpha = K_{eq}\ \alpha_N \tag{2.11}$$

Accurate measurements of the separation factor for the hydrogen-aminomethane exchange have not been made, however studies conducted by A.E.C.L. (13) strongly suggest that it is essentially equal to that for the hydrogen-ammonia system. The separation factor for the hydrogen-ammonia exchange is given as

$$\log \alpha = -0.24218 + \frac{237.59}{T} \tag{2.12}$$

The solubility of potassium methylamide in aminomethane in the temperature range -78 to +40°C was investigated by Hayashitani (14). His results indicated that the solubility increased with decreasing temperature. Values of the solubility at -78 and +25°C were 0.70 and 0.44 mol/l, respectively.

Bar-Eli and Klein (4) used a stirred reactor to study the exchange reaction with a lithium methylamide catalyst. They obtained rate constants of about 3.6 min^{-1} and 6.5 min^{-1} at temperatures of -46 and -29°C, respectively. A linear dependence of the rate of exchange on catalyst concentration was observed up to a concentration of 10 m mol/l, above which the rate was independent of concentration. The activation energy calculated from their data was 15.1 kJ/mol. They also measured the ratio of the rates of exchange, with potassium amide as catalyst, for the ammonia and aminomethane reactions. At -66°C the rate constant for the hydrogen-aminomethane reaction was 35 times that for the hydrogen-ammonia reaction.

Rochard (3) also used a stirred reactor to investigate the kinetics of the exchange with potassium methylamide as catalyst. Table 1 contains the results of her work with the hydrogen-aminomethane system. She determined that the reaction was first order with respect to the concentration of dissolved hydrogen. The activation energy was calculated to be 28.4 kJ/mol. The discrepancy between this value and that obtained by Bar-Eli and Klein was attributed to the use of different values for the hydrogen solubility. At -77.2 and -90°C the rate depended linearly on the catalyst concentration up to about 20 m mol/l. The addition of 0.1 mole percent ammonia to the aminomethane solution had no effect on the measured rate of exchange but the addition of 1.0 percent ammonia decreased the rate by a factor of 10.

Kalra and Otto (2) used a single sphere absorber to obtain data on the hydrogen-aminomethane exchange with potassium methylamide as the catalyst. The temperature range of their investigation was -10 to -30°C. Values of the rate constant for solutions containing catalyst concentrations up to 0.4 m mol/g ranged from 250 to 635 s^{-1}. The dependence of the rate constant on the catalyst concentration was linear up to about 0.13 m mol/g. An activation energy of 16.8 kJ/mol was calculated from their data. It should be noted that the catalyst concentrations were determined by analyzing the solutions for the total potassium concentrations and assuming that all the potassium was present as potassium methylamide.

[illegible] more detailed literature survey on the ammonia and aminomethane-

TABLE 1

CATALYST CONCENTRATIONS AND RATE CONSTANTS MEASURED BY ROCHARD (3) FOR THE HYDROGEN-AMINOMETHANE SYSTEM

C (m mol/l)	k_1 (min^{-1})		
	-62.2 °C	-77.2 °C	-90.0 °C
1.1	5.8		
1.9	10.6	2.9	0.9
2.8	16.3	4.6	1.4
5.9	30.7	9.7	2.8
6.5	32	11.3	
9	55	14.7	
12		18.8	6.8
12.5		19.0	6.3
14	60	19.0	7.0
14		21.5	
18		30	
19.5		27	9.2
20			9.8
20.5		28	
24		35	12.8
26		30	12.0
28		30	
29		31	13.7
35		32	13.2
38		42	16.7
48			18.0
42		41	20.8

hydrogen systems was included in Kalra's thesis (12).

2.3 Mass Transfer and Chemical Reaction on a Single Sphere Absorber

Lynn, Straatemeir and Kramers (15) were the first to use a single sphere absorber for mass transfer studies. To describe the hydrodynamics of the flow of liquid over the sphere, they assumed that the thickness of the liquid film flowing at any latitude on the sphere was the same as that for an equal flowrate per unit length on an inclined plane making the same angle with the vertical. It then followed, from the solution of Nusselt for laminar flow down an inclined plane, that the film thickness was given by

$$\Delta = [\frac{3\nu L}{2\pi R g}]^{1/3} \sin^{-2/3}\theta \tag{2.13}$$

and the velocity distribution could be represented as

$$v_\psi = v_o(1 - (\frac{x}{\Delta})^2) \tag{2.14}$$

where v_o is the velocity at the surface of the film given by

$$v_o = \frac{g\,\Delta^2 \sin\theta}{2\nu} \tag{2.15}$$

Equation (2.14) can also be expressed as

$$v_\psi = \frac{3L}{4\pi R\Delta_1} \sin^{-1/3}\theta\ (1 - (\frac{x}{\Delta})^2) \tag{2.16}$$

where Δ_1 = Film thickness at the equator of the sphere

$= (\frac{3\nu L}{2\pi R g})^{1/3}$

Combination of Equations (2.13) and (2.15) yields

$$v_o = [\frac{9g}{32\pi^2\nu}]^{1/3} L^{2/3} R^{-2/3} \sin^{-1/3}\theta \qquad (2.17)$$

From which the time of exposure of a surface element on the sphere is given by

$$t_{max} = \int_o^{\pi} \frac{Rd\theta}{v_o} = [\frac{9g}{32\pi^2\nu}]^{-1/3} L^{-2/3} R^{5/3} \int_o^{\pi} \sin^{1/3}\theta\, d\theta \qquad (2.18)$$

$$= 2.58[\frac{9g}{32\pi^2\nu}]^{-1/3} L^{-2/3} R^{5/3}$$

The equation describing gas absorption into a film of liquid flowing on a sphere with a first order chemical reaction occurring between the solute and a constituent in the liquid may be obtained by considering the coordinate system shown in Figure 1. The volume element ABCD located in the spherical film is bounded by two streamlines AD and BC and by two radial lines AB and CD. A steady state mass balance on the solute gas in the element may be written as

$$\begin{Bmatrix}\text{Net mass diffusing}\\ \text{into the volume}\\ \text{element}\end{Bmatrix} = \begin{Bmatrix}\text{Net mass}\\ \text{removed by}\\ \text{bulk flow}\end{Bmatrix} + \begin{Bmatrix}\text{Net mass}\\ \text{removed by}\\ \text{chemical}\\ \text{reaction}\end{Bmatrix} \qquad (2.19)$$

Neglecting convection terms in the R and ϕ directions and diffusion terms in the θ and ϕ directions Equation (2.19) may be expressed as

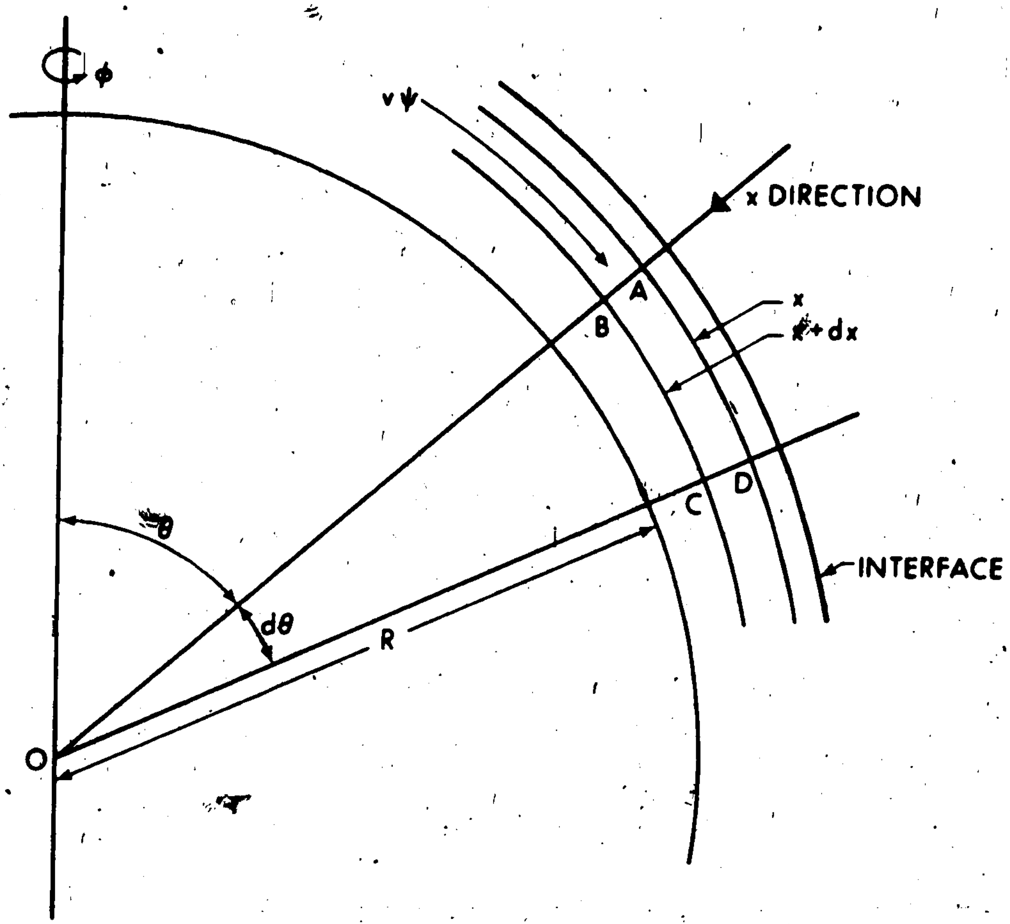

Figure 1: Vertical Section through the Centre of a Sphere

$$2\pi D \sin\theta \left(R^2 \frac{\delta^2 C}{\delta x^2} dx d\theta - 2R \frac{\delta C}{\delta x} dx d\theta\right) = 2\pi R \sin\theta\, v_\psi \left(\frac{\delta C}{\delta\theta}\right)_\psi$$

$$dx d\theta + 2\pi R^2 \sin\theta\, d\theta dx\, k_1 (C - C_o) \qquad (2.20)$$

or

$$DR \frac{\delta^2 C}{\delta x^2} - 2D \frac{\delta C}{\delta x} = v_\psi \left(\frac{\delta C}{\delta\theta}\right)_\psi + Rk_1 (C - C_o) \qquad (2.21)$$

Substitution of the variable $y = \frac{x}{\Delta}$, where $\Delta = \Delta_1 \sin^{-2/3}\theta$, introduces a coordinate system which accounts for the stretching of the liquid film as it flows over the sphere (16). Thus

$$\frac{\delta^2 C}{\delta y^2} - \frac{2D}{\Delta_1 \sin^{-2/3}\theta} \cdot \frac{\Delta_1^2 \sin^{-4/3}\theta}{DR} \frac{\delta C}{\delta y} = (1 - y^2) \frac{v_o \Delta_1^2}{DR}$$

$$\sin^{-4/3}\theta \frac{\delta C}{\delta\theta} + \frac{k_1 \Delta_1^2}{D} \sin^{-4/3}\theta\, (C - C_o) \qquad (2.22)$$

Wild and Potter (17) reduced Equation (2.22) by noting that $\Delta_1/R \simeq 0$ and introducing the following dimensionless variables:

$$d\psi = \frac{RD}{v_o \Delta^2} d\theta = \frac{4\pi R^2 D}{3L\Delta_1} \sin^{5/3}\theta\, d\theta \qquad (2.23)$$

$$M = \frac{k_1 \Delta_1^2}{D} \qquad (2.24)$$

$$C^* = \frac{C - C_o}{C_i - C_o} \qquad (2.25)$$

which yielded

$$\frac{\delta^2 C^*}{\delta y^2} = (1 - y^2)\,\frac{\delta C^*}{\delta \psi} + M \sin^{-4/3}\theta \cdot C^* \qquad (2.26)$$

They used a Crank-Nicholson six point implicit numerical method to obtain a solution to Equation (2.26) with the boundary conditions

$C^* = 1,\ y = 0,\ \psi > 0$

$C^* = 0,\ y = \infty,\ \psi > 0$

$C^* = 0,\ y > 0,\ \psi = 0$

Integration of the interfacial concentration gradient around the sphere yielded the total gas absorption rate G, as

$$G = 2\pi R^2 D \int_0^{\pi} \left(\frac{\delta C}{\delta x}\right)_i \sin\theta \, d\theta \qquad (2.27)$$

$$= \frac{3L}{2} \int_0^{\psi_2} \left(\frac{\delta C}{\delta y}\right)_i d\psi$$

where ψ_2 = Maximum value of ψ, occurring at $\theta = \pi$ for a spherical film

It also followed from Equations (2.18), (2.23) and (2.24) that

$$k_1 t_{max} = \frac{M\psi_2}{0.6628} \qquad (2.28)$$

Wild and Potter developed several simpler equations which approximate their numerical solution within one percent for all possible values of $k_1 t_{max}$. These equations for the case where $C_o = 0$ are

1. for $k_1 t_{max} = 0$ (physical absorption)

$$\frac{G}{LC_i\psi_2^{1/2}} = \left(\frac{9}{\pi}\right)^{1/2} \qquad (2.29)$$

2. for $k_1 t_{max} < 1.0$

$$\frac{G}{LC_i \psi_2^{1/2}} = 0.455\, k_1 t_{max} + 1.693 \qquad (2.30)$$

3. for $1.0 < k_1 t_{max} < 5.0$

$$\frac{G}{LC_i \psi_2^{1/2}} = 1.428 \sqrt{k_1 t_{max}} + \frac{0.689}{\sqrt{k_1 t_{max}}} \qquad (2.31)$$

4. for $5.0 < k_1 t_{max} < 25.0$

$$\frac{G}{LC_i \psi_2^{1/2}} = 1.428 \sqrt{k_1 t_{max}} + \frac{0.54}{\sqrt{k_1 t_{max}}} \qquad (2.32)$$

5. for $k_1 t_{max} > 25.0$

$$\frac{G}{LC_i \psi_2^{1/2}} = 1.428 \sqrt{k_1 t_{max}} \qquad (2.33)$$

Astarita (18) has shown that for the case of high values of the rate constant, Equation (2.33) above, that the total gas absorption rate is independent of the liquid flowrate and is given by

$$G = 4\pi R^2 (C_i - C_o) \sqrt{Dk_1} \qquad (2.34)$$

or

$$k_L = \sqrt{k_1 D}$$

Equation (2.34) is equivalent to Equation (2.33).

3. EXPERIMENTAL

3.1 Apparatus

3.1.1 General

The hydrogen-aminomethane exchange experiment consisted of contacting liquid amine, flowing over the ball absorber, with gaseous hydrogen which was enriched with hydrogen deuteride (HD). The HD diffused from the gas phase to the liquid amine interface where it dissolved and diffused into the liquid. Deuterium atoms of the dissolved hydrogen exchanged with hydrogen atoms of the amine resulting in a slight supersaturation of H_2, which then diffused back to the gas phase. The net result of this process was a reduction of the deuterium concentration in the gas phase.

Since the solubility of hydrogen in aminomethane is very low, the driving force for mass transfer in the liquid phase is small. Consequently the extent to which the deuterium content of the hydrogen would deplete during a single pass by the sphere would be small and difficult to detect. Thus a known volume of hydrogen was continuously recirculated past the sphere so that the depletion of HD was cumulative with time. The amine was fed over the absorber on a once through basis so that the deuterium concentration in the liquid feed was essentially constant with time.

Solutions of PMA and PLMA in aminomethane are corrosive. The equipment in contact with these solutions was constructed of 316 or 304 stainless steel, glass or polypropylene and these materials satisfactorily resisted attack by the amide solutions. Most of the gaskets and O-rings were made of neoprene rubber. The neoprene in contact with the liquid PMA and PLMA solutions became brittle after several experimental runs and had to be replaced. Polypropylene glands were used for all the stainless steel valve packings and polypropylene tubing was used whenever flexible lines in contact with the liquid amide solutions were required.

The stainless steel portions of the equipment were designed for a maximum pressure of 3500 kPa at temperatures less than -200°C. Operating pressures in these sections were never more than 520 kPa and the minimum temperature reached was -55°C. Glass sections were used in those portions of the equipment where visibility was desired. The glass section with the lowest maximum operating pressure had a working pressure of 350 kPa over the temperature range -200 to 300°C. The most extreme condition encountered in these sections was a pressure of 103 kPa at -55°C. These operating conditions left a wide margin for safety.

The amide solutions react violently with oxygen or water, thus precautions were taken to eliminate air and water from the equipment.

3.1.2 Hydrogen-Aminomethane Exchange Apparatus

Figure 2 is a schematic diagram of the exchange apparatus which was used to contact hydrogen, enriched in deuterium, with liquid amine. The exchange apparatus was enclosed in an insulated air bath (9) which could be maintained at a constant temperature, ± 1°C, over the temperature range -10 to -55°C. The refrigeration was provided by a "York" model F62C-502E, six cylinder, two stage refrigerant compressor, rated at 7920 Btu/hr at -100°F. The compressed refrigerant 502 was expanded (12) directly into a cooling coil (13) contained in the air bath. A six kilowatt "Chromalox" electric heater (14) was situated in front of the cooling coil. The power to the heater was controlled with a 240 V, 28 amp power transformer (15) which allowed the air bath

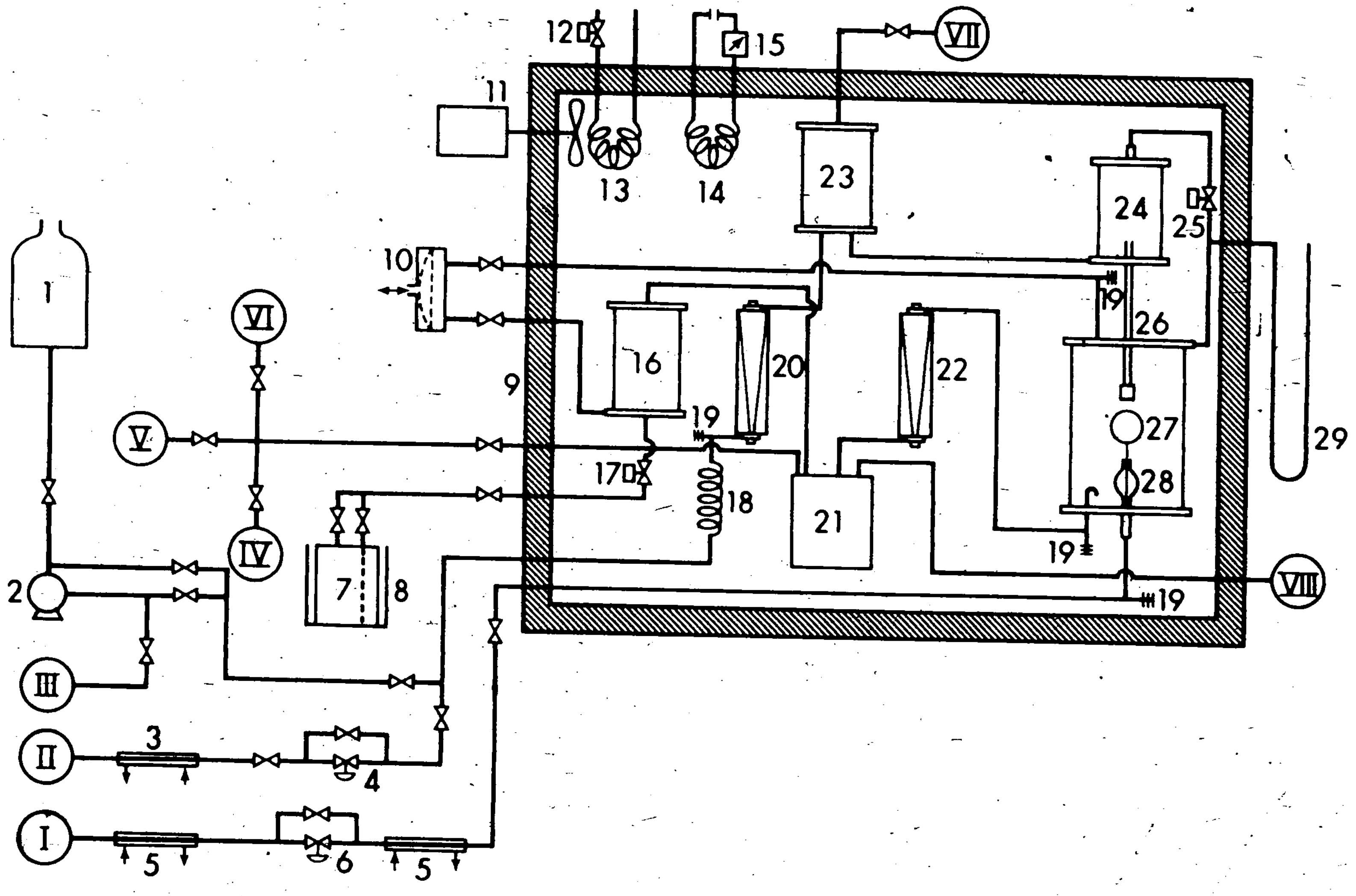

Figure 2: Gas-Liquid Exchange Apparatus

SYMBOLS FOR FIGURE 2

1. Methyl alcohol container
2. Alcohol pump
3. Liquid feed double pipe heat exchanger
4. "Whitey" control valve on liquid feed line
5. Liquid return double pipe heat exchangers
6. "Whitey" control valve on liquid return line
7. Saturator amine storage tank
8. Cold trap for saturator amine storage tank
9. Refrigerated air bath enclosure
10. Gas circulation pump
11. Air bath circulation fan
12. Refrigerant expansion valve
13. Cooling coil
14. Heating coil
15. Variable transformer
16. Gas saturator
17. Solenoid valve
18. In line heat transfer coil
19. Thermocouples
20. Liquid rotameter
21. Gas reservoir
22. Gas rotameter
23. Entrained hydrogen collector
24. Liquid distributor
25. Pressure balance solenoid valve
26. Jet nozzle and liquid approach tube
27. Ball absorber
28. Liquid take off tube
29. Manometer

SYMBOLS FOR FIGURE 2 (continued)

I. To liquid return tanks

II. To liquid feed tanks

III. To alcohol drain

IV. To vacuum system

V. To pressure vent

VI. To enriched hydrogen storage tank

VII. To dissolved hydrogen vent

VIII. To gas sampling system

temperature to be varied over the range mentioned above. A circulating fan (11) was mounted behind the coils to maintain a uniform temperature throughout the air bath.

The feed PMA or PLMA solution entered the exchange apparatus via a 1/4 inch stainless steel tube. An auxiliary refrigeration unit provided the refrigeration for the methanol used as the cooling medium in double pipe heat exchangers located on this tube. The purpose of these exchangers was to cool the amine to prevent evaporation upon contact with warm tubing. The flowrate of the feed was controlled with a 1/4 inch "Whitey" stainless steel union bonnet regulating valve (4). A bypass, through a 1/4 inch "Whitey" stainless steel shut off valve, around the regulating valve was provided to prevent flashing of the amine during startup, which could result in the valve becoming plugged with solid amide.

An in-line heat exchange coil (18) was included on the feed line, inside the air bath, to bring the amine temperature close to the desired reaction temperature. The flowrate of the feed was measured with a rotameter (20). A glass section (23), designed for the removal of entrained hydrogen in the liquid feed, was located upstream of the liquid distributor (24). Both of these sections aided in the elimination of pulsations in the liquid flow and provided the residence time required to bring the liquid to the temperature in the air bath. The top of the distributor was connected to the absorption chamber through a remotely actuated solenoid valve (25), which permitted the pressures in these sections to be equalized. The liquid was fed over the ball absorber (27) through a 1/2 inch diameter stainless steel tube equipped with a 0.046 cm diameter ruby nozzle (26). The ball absorber was a 3.81 cm diameter ball bearing which had been softened by heat treating. The surface of the ball had been roughened to enhance wetting. A 1/16 inch mark machined on the top of the ball aided proper alignment of the jet. The alignment of the jet was accomplished with the use of an eccentric mechanism mounted on the top flange of the absorption chamber. The ball was supported on a 1/8 inch diameter stainless steel rod which also acted as the liquid take-off. This rod was surrounded by a glass take-off tube (28) with an inside diameter of 0.9525 cm. Excellent control of the liquid level in this tube was provided through the use of a "Whitey 21RS4" 316 stainless steel needle valve (6). A bypass was also installed around this valve to prevent flashing of the amine during startup. Concentric pipe heat exchangers (5) were located on the liquid return line to prevent the build up of pressure gradients due to the heating of the return amine (I).

The enriched hydrogen was introduced into the system from a storage cylinder (VI). A gas reservoir (21) provided additional volume so that an appropriate amount of gas could be charged to the system. The hydrogen was circulated through the absorption chamber with a diaphragm pump (10), which was driven by an air motor. A rotameter (22) was used to measure the gas flowrate. The circulating gas passed through a saturator (16) which was partially filled with dry aminomethane. The dry amine was stored in a tank (7) between experiments and was introduced into the saturator via a remotely actuated solenoid valve (17). The purpose of the saturator was to saturate the hydrogen with amine and thus prevent evaporation of the amine flowing over the sphere. The total pressure in the system was measured with a mercury manometer (29). The temperatures of the liquid feed, liquid return and hydrogen (above and below the absorption chamber) were monitored throughout each experimental run through the use of copper Constantan thermocouples (19).

An alcohol wash system was used to clean the apparatus after every run. Methyl alcohol, from a reservoir (1), was pumped (2) through the feed line, over the ball absorber and collected through the return line. The alcohol could also be drained back from the distributor to the alcohol drain (III). A vacuum pump (IV) was employed to remove the alcohol which could not be drained. Often a water wash was required, which was then followed by a second alcohol wash to remove the water. The water was necessary to dissolve potassium hydroxide formed from the reaction between the alcohol and amide.

3.1.3 Amine Feed System

The amine feed system, Figure 3, consisted of two similar tank systems which could be alternated as the feed or receiving tanks. Each set of tanks (1, 1-A), (2, 2-A) consisted of two 6 inch diameter, 316 stainless steel tanks with a total volume of approximately 13 litres. Refrigerated baths (6) containing an ethylene glycol-water mixture kept at -24°C, with the aid of an auxiliary refrigeration unit, provided the necessary cooling for the amine. Concentric tube heat exchangers (3) (4) were located on both the feed and receiving lines to prevent evaporation of the liquid amine in warm lines during start up. A glass wool filter was located on the feed line to remove any solids which might be present in the feed amine. Pressure gauges (7) (8) were connected to each tank set so that each gauge could be used for either set of tanks. Lines leading to the building exhaust system (IV) (VII) were connected to each of the pressure gauge lines. These were used

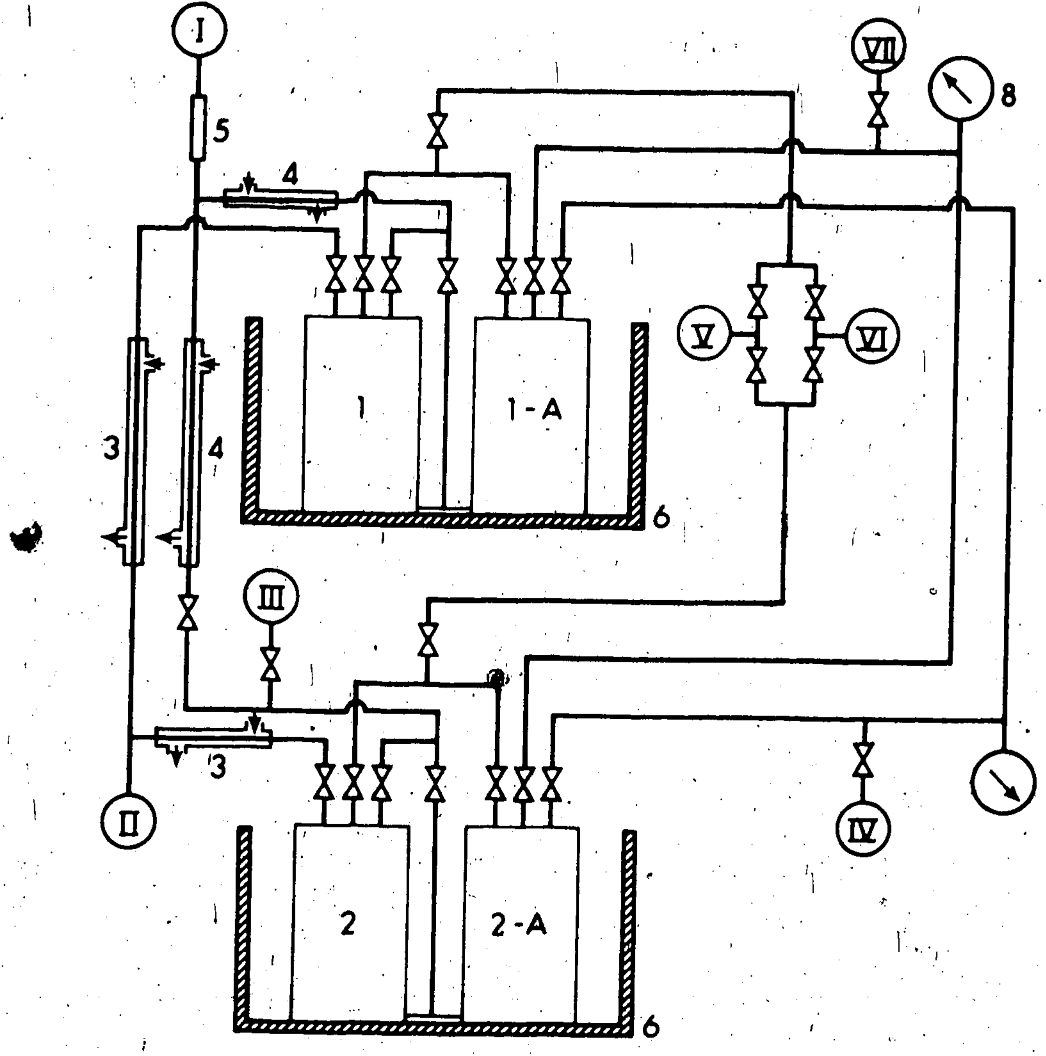

Figure 3: Amine Feed Apparatus

SYMBOLS FOR FIGURE 3

1-1A.	Liquid feed/receiving tanks, set one
2-2A.	Liquid feed/receiving tanks, set two
3.	Concentric tube heat exchangers on return lines
4.	Concentric tube heat exchangers on feed lines
5.	Glass wool filter on feed line
6.	Refrigeration baths
7.	Pressure gauge
8.	Pressure gauge
I.	Amine feed to absorber
II.	Amine return from absorber
III.	Liquid drain line
IV.	Pressure bleed
V.	To hydrogen pressure cylinder
VI.	To vacuum
VII.	Pressure bleed

when vapors were bled off the tanks to reduce pressure.

3.1.4 Gas Sampling System

The gas sampling system, Figure 4, was used to withdraw hydrogen samples, at suitable intervals, from the exchange apparatus for subsequent analysis for the HD concentration. Gas samples were introduced into the sampling system, via a 1/8 inch stainless steel line, by opening a 1/4 inch stainless steel "Whitey" shut off valve (1). The entire sampling system could be evacuated, to prepare for the introduction of a sample, by opening a similar valve (2) connected to a vacuum pump (II). A 2 mm vacuum stopcock (4) isolated the remainder of the sampling system from the initial sample volume (3). The amine vapors contained in the sample were removed in two liquid nitrogen cold traps (5), connected in series. The samples were collected in evacuated glass sample bombs (7) which were connected to the system with a ground glass joint. A 2 mm vacuum stopcock (6) was used to isolate the sample bombs from the system. The absolute pressure of each sample was measured with a mercury manometer (11). Either leg of the manometer could be isolated by closing the appropriate 2 mm vacuum stopcock (8, 9). Prior to the start of an experiment both legs of the manometer were evacuated. Stopcock (9) was then closed to allow the absolute pressure of the samples to be measured.

3.1.5 Catalyst Make Up System

The PMA and PLMA catalyst solutions were made up in a standard twenty-five pound propane tank (1), Figure 5. The tank was fitted with both a dip tube (7) and a tube connected to the top of the tank (6),

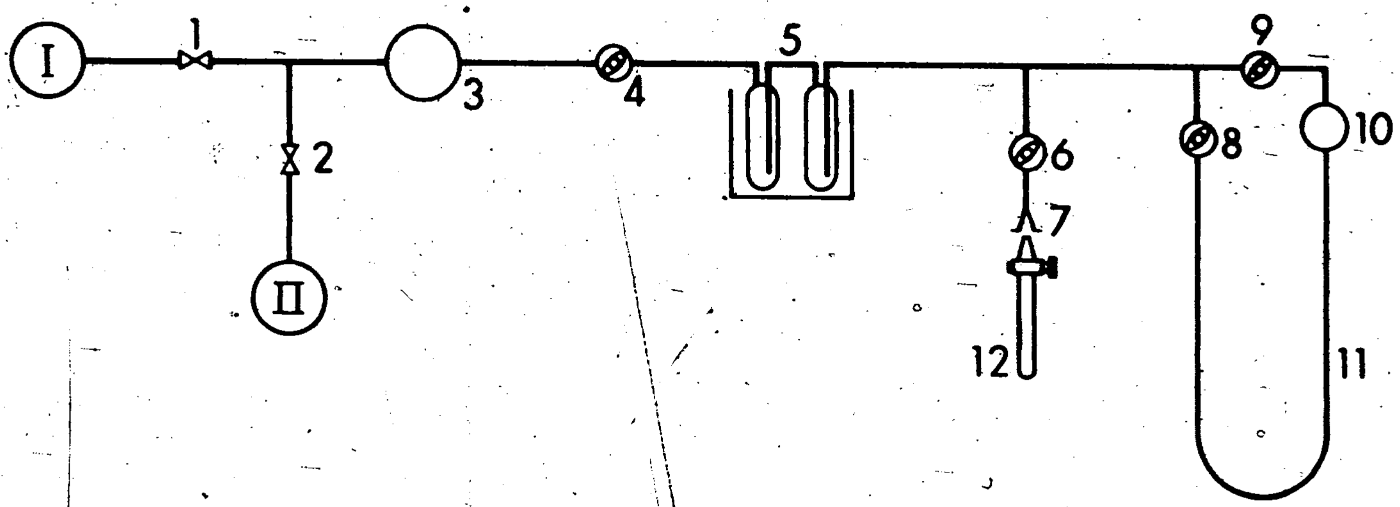

Figure 4: Gas Sampling System

SYMBOLS FOR FIGURE 4

1. Valve isolating sampling system from exchange apparatus
2. Valve isolating sampling system from vacuum pump
3. Additional sample volume
4. Glass valve isolating sample volume from the remainder of the sampling apparatus
5. Liquid nitrogen cold traps for the removal of amine
6. Glass valve isolating sample system from the sample bomb
7. Ground glass joint

8,9. Glass valves on either side of the sample pressure manometer

10. Additional volume to prevent mercury from entering the sampling apparatus
11. Manometer
12. Sample bomb

I. To gas reservoir on exchange apparatus

II. To vacuum pump

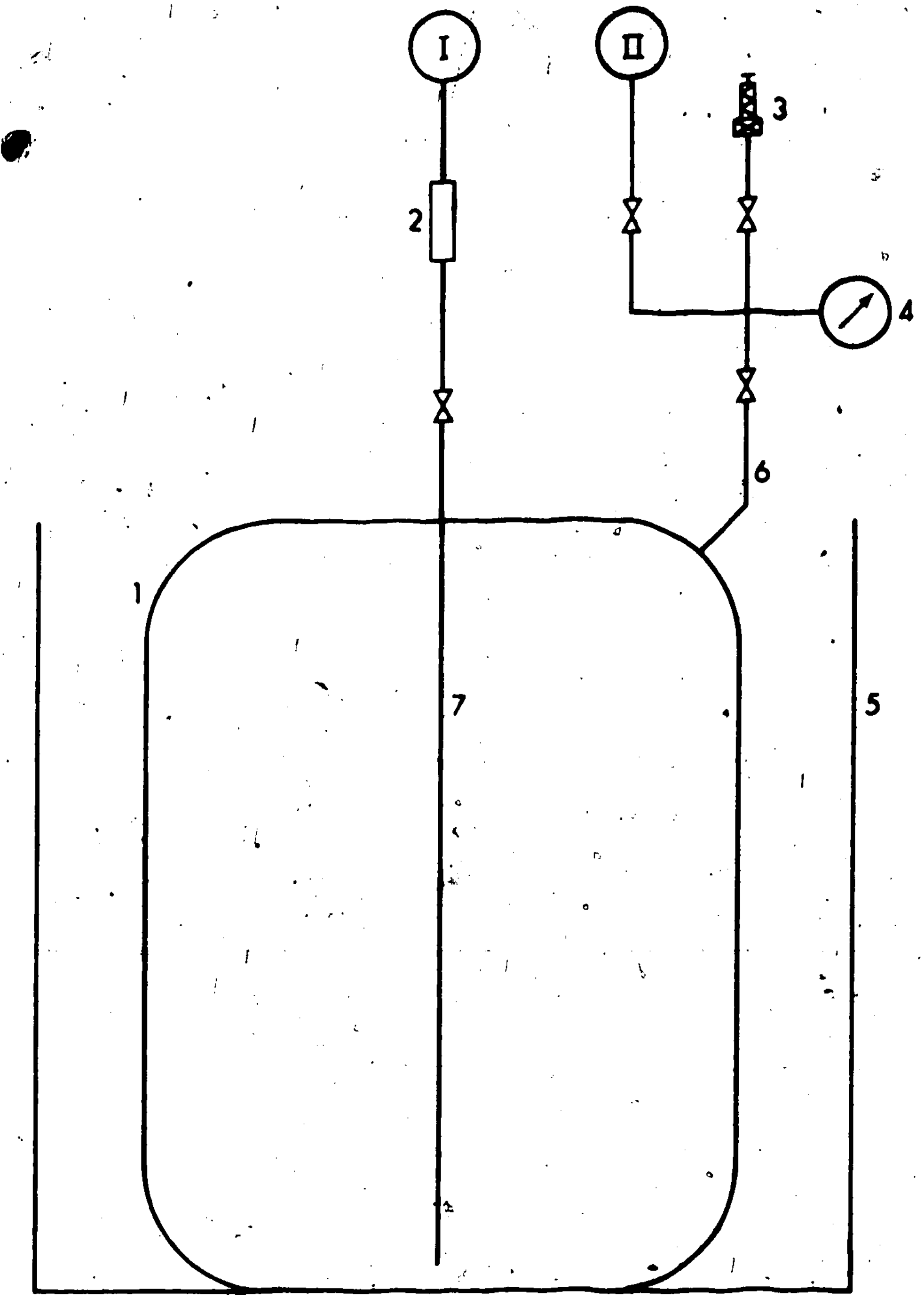

Figure 5: Catalyst Make Up Apparatus

SYMBOLS FOR FIGURE 5

1. Standard twenty-five pound propane tank
2. Filter
3. Relief valve
4. Pressure gauge
5. Liquid nitrogen bath
6. Vapor line
7. Liquid line

I. To liquid feed tanks
II. To dry amine tank

which enabled the contents to be withdrawn or introduced as either a liquid or a vapor. Freshly cut potassium and lithium were introduced through the top hole of the tank. Dry amine was then distilled onto the potassium and lithium by submerging the tank in liquid nitrogen contained in a bath (5) surrounding the tank. The alkali metals subsequently reacted with the amine producing their respective amides and hydrogen, which resulted in an increase in the pressure in the tank. The pressure could be monitored with a pressure gauge (4) connected to the vapor line. A relief valve (3) set to relieve at 550 kPa was also connected to this line to protect the tank from a possible rupture due to excessive pressure. A 60 micron "Hoke" sintered stainless steel filter (2) was installed on the liquid line and used to remove solids contained in the catalyst solution.

3.1.6 Gas Analysis

The hydrogen samples taken during the exchange experiment were analyzed for their deuterium concentrations on a mass spectrometer, which was designed and constructed by Buckley (19). The spectrometer consisted of a 90° sector analyzer, which employed dual detection cups for the simultaneous collection of the H_2 and HD isotopes. The signals from these cups were amplified and displayed on "Cary" model 401 vibrating reed electrometers. These signals were also read and processed, to give the ppm of HD in the sample, by the Department's IBM 1800 computer. These results were subsequently compared with the ppm values of standards of known concentration to yield the actual concentrations of HD in the sample. The precision of this analysis was ± 2 ppm.

3.1.7 Hydrogen Make Up

The hydrogen used in the exchange experiment was generated by electrolyzing water in a "Milton Roy" hydrogen generator. A small amount of D_2O was added to the feed water for the generator to yield hydrogen with a deuterium concentration in the order of a D/(D+H) atom ratio of 500 ppm.

3.2 Experimental Procedure

3.2.1 The Exchange Experiment

The exchange experiment consisted of contacting gaseous hydrogen with a liquid solution of PMA or PLMA in aminomethane on a 3.81 cm diameter ball absorber. A step by step operating procedure for a typical experimental run is given in Appendix A.

Enriched hydrogen, from a storage cylinder, was introduced into the exchange apparatus via a "Matheson Model 70A" low pressure regulator prior to the start of a run. This gas was circulated with a diaphragm pump at a rate of about 50 cm^3/s. The total gas volume was approximately 2500 cm^3, resulting in a turn around time of about 50 seconds. The hydrogen was saturated with amine, to prevent evaporation of the liquid feed on the absorber, by passing it through a glass section containing dry liquid amine.

The exchange experiment was operated at a hydrogen partial pressure of about 162 kPa and the amount of amine feed was such that the liquid to gas molar ratio was in the order of 200. The enrichment of the amine under these conditions was less than one ppm during a run.

The liquid solution was stored in the feed tanks which were maintained at approximately -25°C. During an experimental run the pressure in the feed tanks was raised to about 275 kPa with ultra high purity hydrogen, to provide the necessary pressure gradient required to feed the liquid into the absorption chamber. This hydrogen was kept in a high pressure cylinder which was connected via a "Matheson" regulator to the top of the feed tanks. The liquid flowrate was controlled at about 0.25 cm^3/s with the "Whitey" regulating valve. This flowrate was sufficient to ensure that the enrichment of the liquid on the absorber was minimal. There was no visual evidence of ripples on the liquid surface at this flowrate; however ripples could be seen at higher flowrates.

The liquid was passed through a heat transfer coil located inside the refrigerated air bath, to bring its temperature close to the absorber temperature. Any undissolved hydrogen contained in the liquid feed was removed in a glass section which was located upstream of the liquid distributor. At the beginning of a run this section was partially filled with liquid solution. The remaining feed entered and exitted through the bottom of this section and the free hydrogen rose to the top, providing a feed stream which was entirely liquid.

Fluctuations in the liquid flow were damped in the liquid distributor before admission to the absorber. The liquid level in the distributor was adjusted during start up by opening the remotely actuated solenoid valve and allowing the liquid to rise to the desired level. The solenoid valve was then closed and the liquid flowrate was adjusted to the proper value. A laminar jet was used to introduce the liquid feed onto the ball absorber. The jet diameter was 0.046 cm and jet lengths of 0.255 to 0.390 cm were used throughout the entire study.

The work of Kalra and Otto (2) indicated that a stagnant layer on the take-off liquid extended to the junction of the take-off rod and the ball providing the take-off length was 1.25 cm. The take-off length was maintained at this value by controlling the return liquid flowrate with the "Whitey" needle valve. Small disturbances were observed in the liquid in the take-off tube indicating the possibility of some activity. Since the diameter of the sphere was 24 times the diameter of the rod any exchange occurring in the take-off level was assumed negligible.

Gas samples were taken throughout the experiment at intervals ranging from 600 to 1000 seconds. Shorter intervals were used at the higher temperatures and during the initial part of a run, when higher exchange rates were expected. Sufficient time (400 seconds) was allowed after the liquid entered the absorber to adjust the levels in the distributor and the take-off tube, prior to taking the first sample. The prevented the unsteady conditions in the apparatus during start up from affecting the measured exchange rate. The gas samples were obtained by expanding a 5 cm^3 sample into an evacuated glass sample bomb. An equivalent size sample was discarded immediately before sampling to eliminate the effects of dead volume in the sample lines.

The important variables which were controlled during an experimental run were the gas and liquid flowrates, take-off height and system temperature. Both flowrates and temperatures were recorded after each sample was taken.

3.2.2 Catalyst Solution Make-Up and Analysis

Potassium and lithium metals are extremely hazardous to work with, which necessitates the adherence to safe working procedures.

Hayashitani (14) has outlined the methods recommended when working with these metals. The most important precaution is that contact with air or water must be avoided.

The aminomethane, obtained from Matheson of Canada Ltd., contained a maximum 0.8 weight percent water. This was removed by contacting the amine with an excess of lithium prior to using it to prepare a catalyst solution. The method used for water removal is similar to that for the catalyst make-up, described below.

The propane tank used for the catalyst make-up was initially cleaned and evacuated. A slight positive pressure of argon was then put in the tank to provide an inert, heavier than air atmosphere for the introduction of the potassium or lithium. The oxide layer on the alkali metals was scraped off under mineral oil. The clean metal was then cut into small pieces to enhance the rate of solution in the amine. These pieces were washed in normal pentane to remove the mineral oil and then put in the tank. The argon and the pentane were removed under vacuum prior to the introduction of the aminomethane.

The aminomethane was transferred into the catalyst make-up tank by a simple flash distillation. This was accomplished by immersing the make-up tank in liquid nitrogen and connecting the vapor line to the tank containing the dry amine. The dry amine tank was weighed before and after the distillation so that the correct amount of amine could be transferred into the make-up tank.

The potassium and lithium initially dissolve in the amine and subsequently react to yield the catalyst. The rate of this process is controlled by the solution step. The reactions, described by the following equations

$$CH_3NH_2 + K \rightarrow CH_3NHK + 1/2H_2 \qquad (3.1)$$

and

$$CH_3NH_2 + Li \rightarrow CH_3NHLi + 1/2H_2 \qquad (3.2)$$

are catalyzed by traces of iron supplied by the tank walls. As the reaction proceeds an increase in the pressure, due to the production of hydrogen, is observed which in turn inhibits the rate of reaction. This hydrogen was periodically bled off through the relief valve so that the reaction could proceed at a reasonable rate. The reaction was assumed to have gone to completion when no further increase in pressure was observed. A detailed procedure for the catalyst make-up is included in Appendix A.

The analysis of the catalyst solutions was performed by Raylo Chemicals Ltd. Atomic absorption spectroscopy was used to determine the total K^+ and Li^+ concentrations. Gas chromatography and nuclear magnetic resonance spectroscopy were employed to determine the NH_2^-, CH_3NH^- and dimethylformamidine ($CH_3NHCH = N - CH_3^-$) concentrations. The presence of dimethylformamidine indicated that some decomposition of the amide catalyst had taken place. It is not a catalyst for the exchange reaction.

3.2.3 Gas Analysis

The hydrogen samples taken during an experimental run were analyzed for the concentrations of deuterium with a mass spectrometer. Standards containing D/D+H atom fractions of 1.5, 99, 365 and 471 ppm were used to calibrate the spectrometer, both before and after the analysis of a set of samples. The absolute values of the deuterium concentrations of the samples were determined by comparing the measured values with the measured values of the standards using the following relationships.

$$\delta_{DI} = (\frac{R^*}{R_{st}} - 1)\ 1000 \tag{3.3}$$

$$\delta_{st} = (\frac{C^*_1}{C_{st}} - 1)\ 1000 \tag{3.4}$$

where R^* = The ratio of mass three (HD) to mass two (H_2) currents (I_3/I_2) at a fixed value of I_2. This ratio was uncorrected for the H_3^+ contribution to the mass three signal.

R_{st} = The I_3/I_2 ratio for the principal standard at the same value of I_2.

C^*_1 = The absolute deuterium concentration of the sample (D/D+H in ppm)

C_{st} = The absolute deuterium concentration of the principal standard (D/D+H in ppm)

The 365 ppm standard was arbitrarily chosen as the principal standard for this study. A plot of the δ_{DI} versus δ_{st} values of the standards constituted the calibration curve for the mass spectrometer. The equation for this curve, which was essentially a straight line, was determined by a standard least squares technique. Equation (3.3) was used to convert the measured R^* values of the samples to their corresponding δ_{DI} values. The least squares equation was then used to determine the δ_{st}'s, from which the absolute concentrations were calculated with Equation (3.4).

3.2.4 Method of Interpretation of Data

During an experimental run the number of moles of HD in the gas phase depletes cumulatively with time. This rate of depletion can be expressed as

$$G_i = n_{H_2} \frac{dy}{dt} = \frac{P_{H_2} V}{R_g T} \frac{dy}{dt} \qquad (3.5)$$

where G_i = Instantaneous gas absorption rate (mol/s)

n_{H_2} = Total number of moles of hydrogen gas

y = $[HD]/([HD] + [H_2])$

t = Time (s)

P_{H_2} = Partial pressure of hydrogen (kPa)

V = Total volume of the system occupied by gas (cm^3)

R_g = Universal gas constant $\left(\frac{8315\ cm^3\ kPa}{mol\ \ K}\right)$

T = Absolute temperature of the gas (K)

The interfacial area of contact for the sphere may be corrected for the thickness of the liquid film using the relation

$$\frac{A_A}{A_s} = 1 + \frac{2.58\ \Delta_1}{R} \qquad (3.6)$$

where A_A = Corrected surface area (cm^2)

A_s = Surface area of the dry sphere (cm^2)

Δ_1 = Film thickness at the sphere equator (cm)

R = Radius of the sphere (cm)

The total interfacial area is the corrected surface area plus the area of the laminar jet (A_J), expressed as

$$\begin{aligned} A_T &= A_A + A_J \\ &= A_A + \pi d_J \ell \end{aligned} \tag{3.7}$$

The rate of depletion may be equated to the instantaneous rate of absorption of HD in the amide solution flowing on the sphere to yield

$$-\frac{P_{H_2} V}{R_g T} \frac{dy}{dt} = K_L A_T (C^* - C_e) \tag{3.8}$$

where K_L = Overall mass transfer coefficient (cm/s)

C^* = Concentration of HD in the liquid phase in physical equilibrium with the HD concentration in the bulk gas phase $(\frac{mol}{cm^3})$

C_e = Concentration of HD in the liquid phase in chemical equilibrium with the concentration of CH_3NHD in the bulk liquid $(\frac{mol}{cm^3})$

The concentration of CH_3NHD in the bulk liquid was assumed constant for a given experiment. This assumption implied that C_e was also a constant.

The solubility of HD in aminomethane may be represented by Henry's law as

$$y\, P_{H_2} = P_{HD} = Hx \tag{3.9}$$

or

$$x = \frac{y\, P_{H_2}}{H},$$

where H = Henry's law coefficient $(\frac{kPa}{\text{mole fraction}})$

x = Mole fraction of HD in the liquid phase

Noting that

$$C^* = \rho_L x^* \tag{3.10}$$

and

$$C_e = \rho_L x_e$$

where ρ_L = Molar density of the liquid $(\frac{mol}{cm^3})$

Equation (3.8) may be represented as

$$-\frac{P_{H_2} V}{R_g T}\frac{dy}{dt} = K_L A_T \rho_L \frac{P_{H_2}}{H}(y^* - y_e) \tag{3.11}$$

Setting the mole fraction of HD in the gas at time t = 0 equal to y_{in} and replacing y^* by y, integration of Equation (3.11) from 0 to t yields

$$\ln\left(\frac{y - y_e}{y_{in} - y_e}\right) = \frac{-K_L A_T \rho_L R_g T}{HV} t \tag{3.12}$$

A plot of $\ln(\frac{y - y_e}{y_{in} - y_e})$ versus t results in a straight line with a slope of $\frac{-K_L A_T \rho_L R_g T}{HV}$, from which K_L can be determined.

The total resistance to mass transfer may be represented by the two film theory as

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{\rho_L}{H\, k_G} \tag{3.13}$$

where k_L = Liquid phase mass transfer coefficient $(\frac{cm}{s})$

k_G = Gas phase mass transfer coefficient $(\frac{mol}{cm^2\ s\ kPa})$

The diffusivities of HD in H_2 and of HD in CH_3NH_2 vapor can be estimated using the Wilke-Lee modification of the Hirshfelder-Bird-Spotz method shown below.

$$D_{AB} = \frac{(0.00107 - 0.000246\sqrt{1/M_A + 1/M_B})T^{3/2}\sqrt{1/M_A + 1/M_B}}{P_t(r_{AB})^2\,[f(KT/\varepsilon_{AB})]} \qquad (3.14)$$

where D_{AB} = Diffusivity (cm^2/s)

M_A, M_B = Molecular weight of A and B respectively

P_t = Absolute pressure (atm)

r_{AB} = Molecular separation at collision (Å)

ε_{AB} = Energy of molecular interaction (ergs)

= $\sqrt{\varepsilon_A \varepsilon_B}$

k = Boltzmann's constant

$f(KT/\varepsilon_{AB})$ = Collision function

The diffusivity of HD in the gas phase may then be calculated using

$$D_{mix} = \frac{1}{\dfrac{y_{H_2}}{D_{HD-H_2}} + \dfrac{y_{CH_3NH_2}}{D_{HD-CH_3NH_2}}} \qquad (3.15)$$

where D_{mix} = Diffusivity of HD in the H_2-CH_3NH_2 mixture (cm^2/s)

The geometry of the absorber and the operating conditions were such that the flow of gas was uniform over the sphere at a velocity of approximately 1.1 cm/s. The value of D_{mix} calculated with Equation (3.15) was substituted into Froessling's (20) equation for forced convection mass transfer to single spheres, from which the gas film mass transfer coefficient was determined as follows

$$\frac{2k_C R}{D_{mix}} = 2.0\,[1 + 0.276\,R_e^{1/2}\left(\frac{\mu}{\rho_G D_{mix}}\right)^{1/3}] \qquad (3.16)$$

and

$$k_C = k_G R_g T$$

where k_C = Mass transfer coefficient $\left(\frac{\text{mol}}{\text{s cm}^2 \text{ mol/cm}^3}\right)$

R_e = Gas phase Reynolds number $\left(\frac{2 R v_{av} \rho_G}{\mu}\right)$

μ = Viscosity of the gas mixture (g/cm s)

ρ_G = Density of the gas mixture (g/cm^3)

v_{av} = Average velocity of the gas in the absorption chamber (cm/s)

The values of K_L and k_G calculated in Equations (3.12) and (3.16) respectively, may be substituted into Equation (3.13) to yield a value of k_L. The rate of mass transfer to the liquid may be expressed in terms of k_L as

$$G_i = k_L A_T (C_i - C_e) \tag{3.17}$$

where C_i = Actual HD concentration in the liquid at the interface $\left(\frac{\text{mol}}{\text{cm}^3}\right)$

The hydrogen-aminomethane exchange can be described by the following reversible reaction in the region of low deuterium concentration

$$CH_3NH_2 + HD \rightleftarrows CH_3NHD + H_2 \tag{1.1}$$

At low deuterium concentrations the concentrations of CH_3NH_2 and H_2 may be considered invariant, indicating that the exchange may be represented by the pseudo first order reaction

$$HD \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3NHD \tag{3.18}$$

The local rate of reaction may then be represented as

$$r = k_1' C_{HD} - k_2 C_{CH_3NHD} \qquad (3.19)$$

$$= k_1 (C - C_e)$$

where C = Concentration of HD in the liquid $(\frac{mol}{cm^3})$

Thus Equation (3.17) may be used with the appropriate expression, Equations (2.29) to (2.33), to isolate k_1 as a function of k_L and known system properties. The correct equation was determined by evaluating $k_1 t_{max}$ and comparing its magnitude with the range of $k_1 t_{max}$ for which the above equations apply. For the fast reaction regime, $k_1 t_{max} > 25$,

$$G_1 = A_T (C_1 - C_e)\sqrt{Dk_1} \qquad (2.34)$$

$$= k_L A_T (C_1 - C_e)$$

and

$$k_L = \sqrt{Dk_1}$$

4. RESULTS

The single sphere absorber was used to measure the rates of exchange of hydrogen with PMA and PLMA solutions. Two solutions, with concentrations of 0.31 and 0.40 m mol PMA/g amine were investigated. Experiments were conducted with PLMA solutions, containing a molar ratio of lithium to potassium methylamide of approximately 1:1, at three concentrations of the amides ranging from 0.30 to 0.63 m mol/g amine. Solutions with lithium to potassium ratios ranging from 0.5:1 to 4.2:1 were studied to determine the effect of the Li/K ratio on the exchange rate.

The rate constants and mass transfer coefficients, calculated for each experiment following the procedure given in the previous chapter, are shown in Table 2. Appendix C contains a detailed summary of the experimental and calculated data. All but four of the experiments were conducted under conditions in which the reaction occurred in the fast regime ($k_1 t_{max} > 25$). The experiments which did not occur in the fast regime were those conducted with the solution which had an Li/K ratio of 4.26:1 and the lowest temperature run with the solution which had a Li/K ratio of 1.72:1.

A slight decomposition of the catalysts was indicated in the analyses of several of the aminomethane solutions by the presence of NH_2^- and $CH_3NHC = NCH_3^-$ ions. The concentrations of PMA and LMA in these solutions were taken as the proportion of the potassium and lithium concentrations which could be attributed to the total $CH_3NH_2^-$ concentration. The analyses of the amide solutions obtained from Raylo Chemicals Ltd. are included in Appendix D.

Values of the activation energy for each data set are given

TABLE 2

KINETIC DATA FOR HYDROGEN-AMINOMETHANE EXCHANGE

Date	Temperature (°C)	Catalyst Concentration (m mol/g amine) PMA	LMA	Rate Constant (s^{-1})	Overall Liquid Phase Transfer Coefficient (cm/s)	Liquid Phase Transfer Coefficient (cm/s)	$k_1 t_{max}$
5/6/74	-41.9	0.31	0.0	132	0.0937	0.0947	142
18/6/74	-25.4	0.31	0.0	364	0.1765	0.1817	352
27/6/74	-38.1	0.31	0.0	183	0.1141	0.1157	213
11/7/74	-21.2	0.31	0.0	462	0.2043	0.2115	537
12/7/74	-52.9	0.31	0.0	64.4	0.0592	0.0595	85
5/2/75	-24.8	0.30	0.30	137	0.1102	0.1122	135
6/2/75	-32.8	0.30	0.30	95.3	0.0864	0.0874	90
14/2/75	-38.7	0.30	0.30	62.8	0.0669	0.0674	72
6/3/75	50.6	0.30	0.30	27.3	0.0395	0.0397	35
6/3/75	-51.5	0.30	0.30	29.2	0.0405	0.0407	77
15/3/75	-17.0	0.30	0.30	214	0.1450	0.1490	202
5/4/75	-39.1	0.43	0.43	63.6	0.0670	0.0675	68
11/4/75	-17.8	0.43	0.43	214	0.1441	0.1481	199

continued ...

TABLE 2 (continued)

Date	Temperature (°C)	Catalyst Concentration (m mol/g amine) PMA	LMA	Rate Constant (s^{-1})	Overall Liquid Phase Transfer Coefficient (cm/s)	Liquid Phase Transfer Coefficient (cm/s)	$k_1 t_{max}$
23/4/75	-45.7	0.43	0.43	39.5	0.0498	0.0501	45
21/5/75	-44.6	0.63	0.63	51.3	0.0573	0.0577	58
27/5/75	-47.5	0.63	0.63	46.5	0.0531	0.0534	54
4/6/75	-23.1	0.63	0.63	193	0.1319	0.1350	178
1/7/75	-13.2	0.63	0.63	307	0.1766	0.1834	261
9/7/75	-40.0	0.63	0.63	72.5	0.0709	0.0715	78
30/7/75	-43.2	0.39	1.66	2.1	0.0140	0.0140	2.3
15/8/75	-19.2	0.39	1.66	11.5	0.0343	0.0346	11
29/8/75	-26.4	0.39	1.66	7.5	0.0267	0.0268	7
26/9/75	-48.4	0.40	0.0	101	0.0772	0.0779	119
1/10/75	-20.1	0.40	0.0	582	0.2297	0.2397	592
4/10/75	-40.0	0.40	0.0	164	0.1061	0.1076	188
9/10/75	-29.6	0.40	0.0	303	0.1563	0.1602	312

continued ...

TABLE 2 (continued)

Date	Temperature (°C)	Catalyst Concentration (m mol/g amine) PMA	LMA	Rate Constant (s^{-1})	Overall Liquid Phase Transfer Coefficient (cm/s)	Liquid Phase Transfer Coefficient (cm/s)	$k_1 t_{max}$
10/10/75	-47.7	0.50	0.86	17.5	0.0325	0.0327	22
5/11/75	-20.6	0.50	0.86	87.8	0.0913	0.0928	83
17/11/75	-31.1	0.50	0.86	54.5	0.0666	0.0671	57
21/11/75	-38.1	0.50	0.86	41.3	0.0546	0.0550	46
27/11/75	-10.2	0.50	0.86	161	0.1319	0.1358	141
11/2/75	-45.0	0.48	0.35	54.5	0.0588	0.0592	67
19/2/76	-23.7	0.48	0.35	208	0.1360	0.1393	203
23/2/76	-36.1	0.48	0.35	107	0.0889	0.0899	122
27/2/76	-13.1	0.48	0.35	381	0.1964	0.2045	361
9/3/76	-48.3	0.50	0.25	62.5	0.0610	0.0614	84
12/3/76	-12.2	0.50	0.25	447	0.2130	0.2229	402
17/3/76	-22.6	0.50	0.25	312	0.1670	0.1719	328

in Table 3. These were calculated from a linear least squares fit to the Arrhenius model,

$$k_1 = Ae^{-\frac{E}{R_g T}} \tag{4.1}$$

The natural logarithms of the rate constants are plotted versus the reciprocal of the absolute temperatures for each catalyst concentration on Figures 6 to 14.

TABLE 3

CALCULATED VALUES OF THE ACTIVATION ENERGY

Catalyst Concentration (m mol/g amine)		Activation Energy
PMA	LMA	(kJ/mol)
0.31	-	28.9
0.30	0.30	28.1
0.43	0.43	29.0
0.63	0.63	27.7
0.39	1.66	34.7
0.40	-	29.1
0.50	0.86	27.8
0.48	0.35	29.5
0.50	0.25	27.2

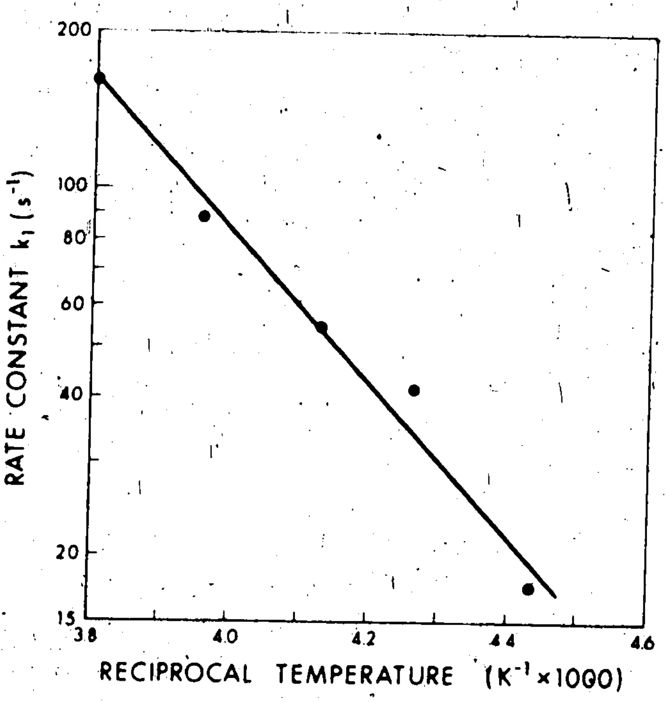

Figure 6: Variation of the Kinetic Rate Constant with Temperature,
[PMA] = 0.5 m mol/g [LMA] = 0.86 m mol/g

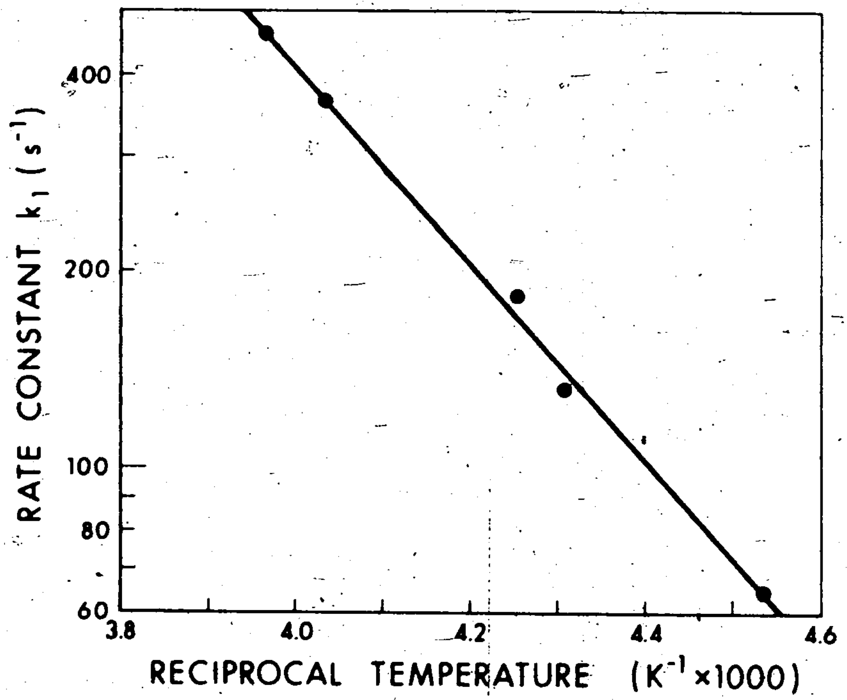

Figure 7: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.31 m mol/g [LMA] = 0 m mol/g

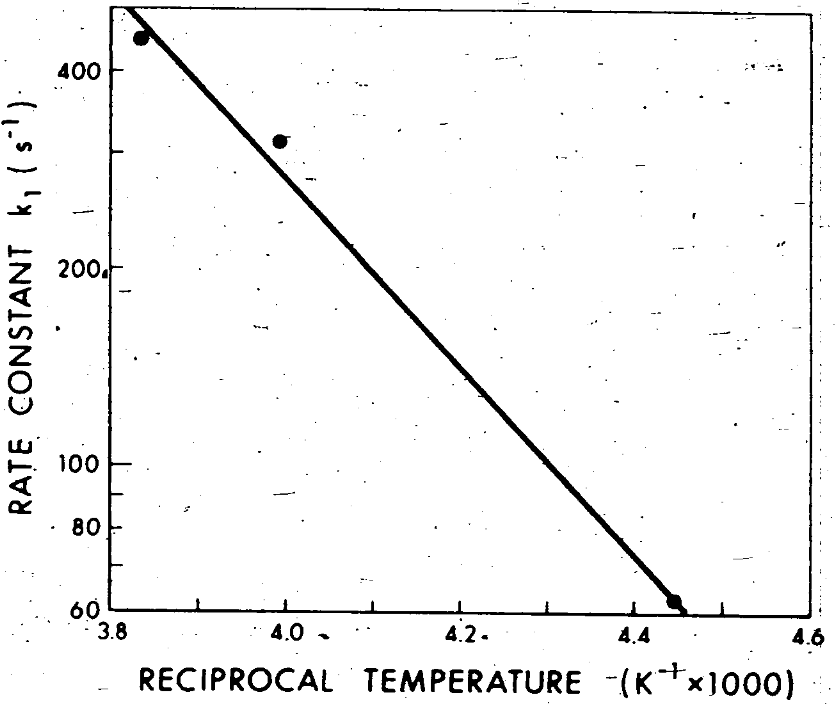

Figure 8: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.5 m mol/g [LMA] = 0.25 m mol/g

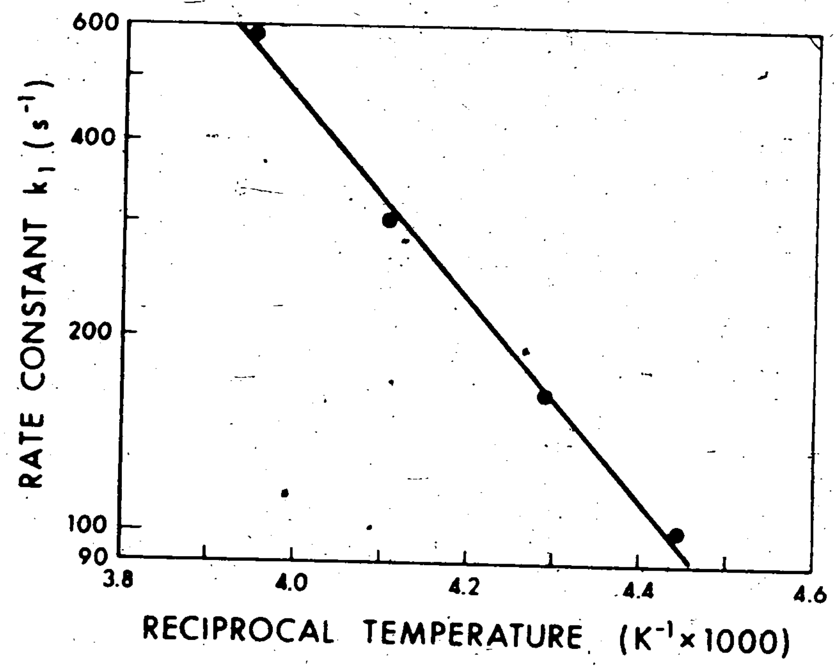

Figure 9: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.4 m mol/g [LMA] = 0.0 m mol/g

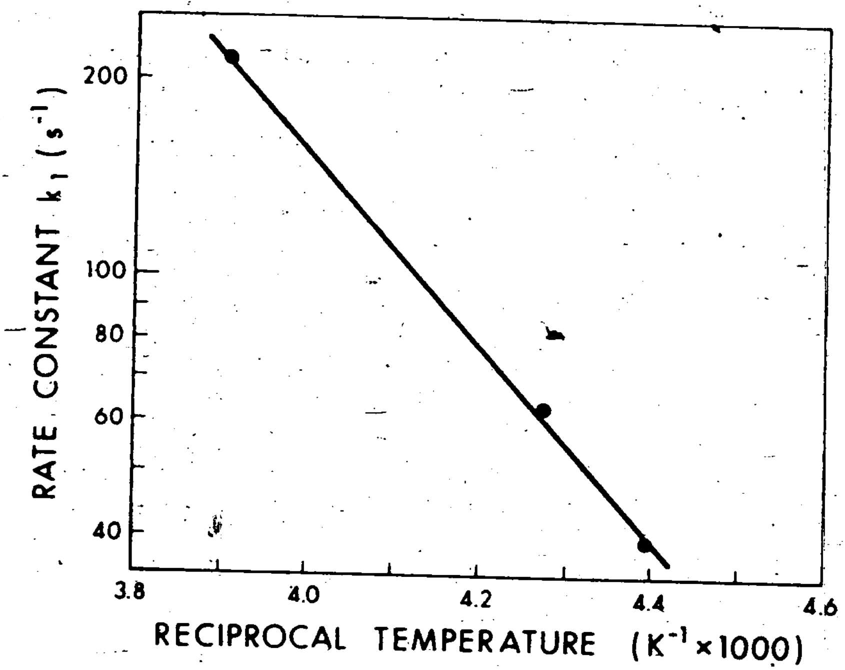

Figure 10: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.43 m mol/g [LMA] = 0.43 m mol/g

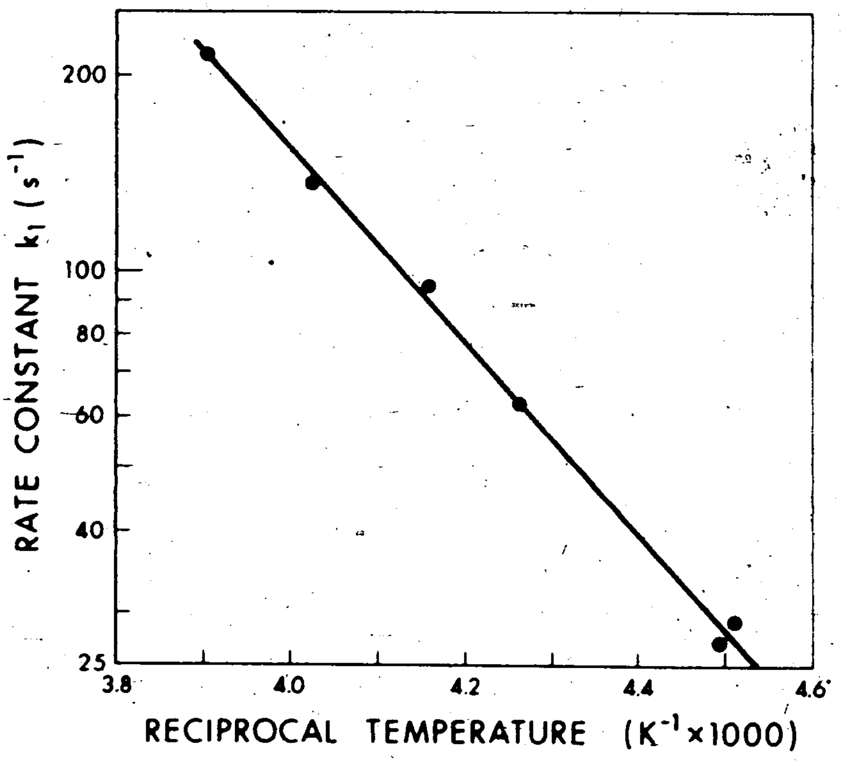

Figure 11: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.3 m mol/g [LMA] = 0.3 m mol/g

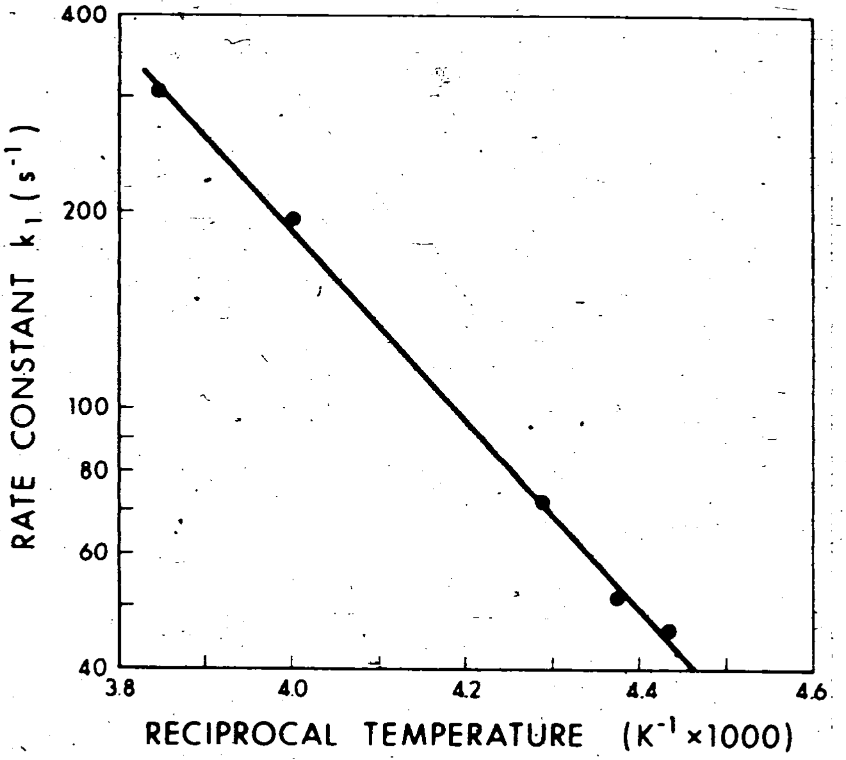

Figure 12: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.03 m mol/g [LMA] = 0.63 m mol/g

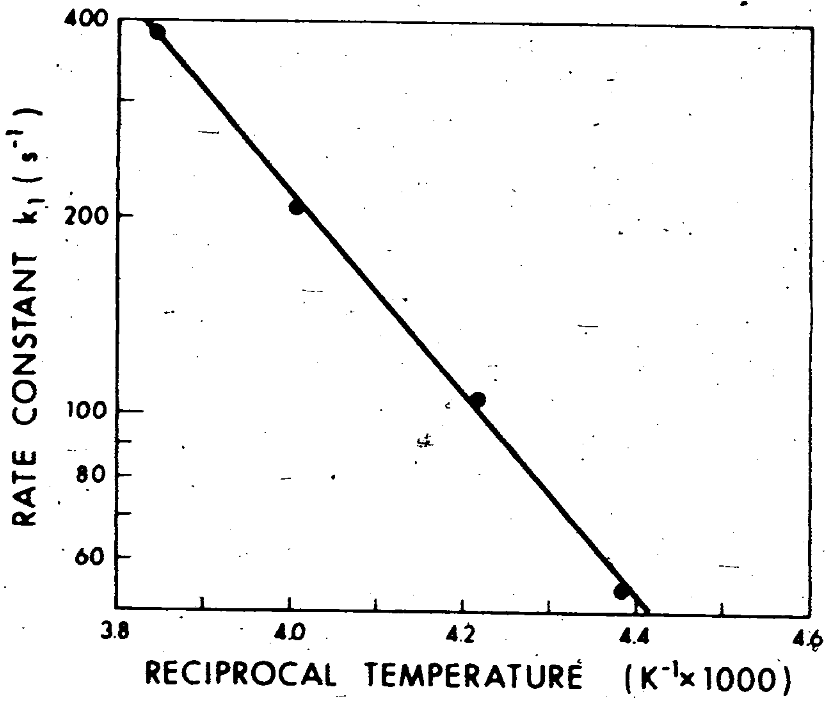

Figure 13: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.48 m mol/g [LMA] = 0.35 m mol/g

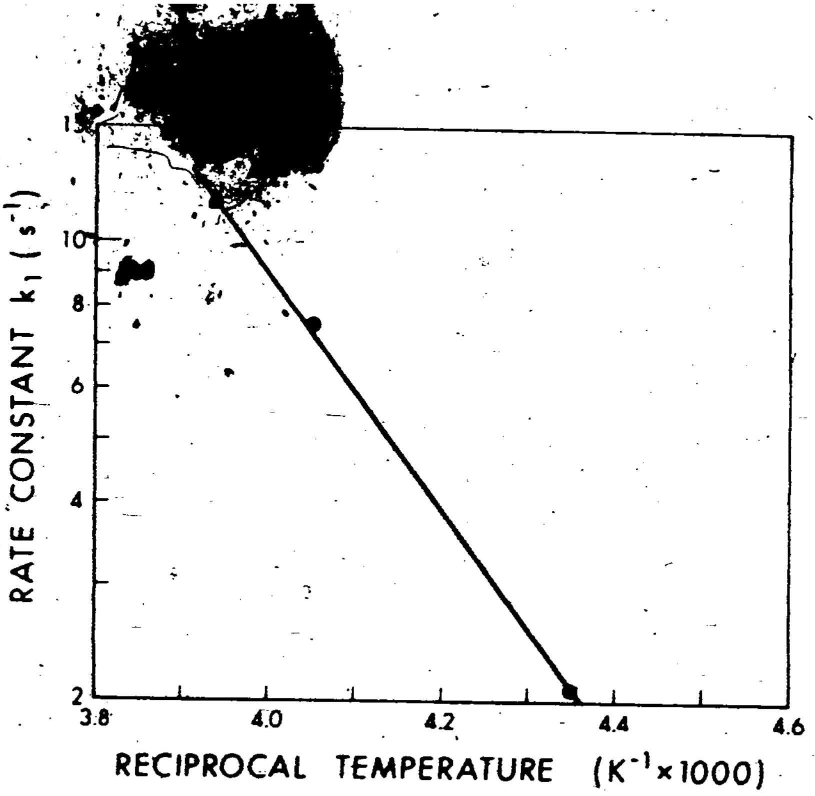

Figure 14: Variation of the Kinetic Rate Constant with Temperature, [PMA] = 0.39 m mol/g [LMA] = 1.66 m mol/g

5. DISCUSSION OF RESULTS

5.1 Effect of Temperature on k_1

The values of the activation energies, shown in Table 3, with the exception of that for the solution which contained a lithium to potassium ratio of 4.26:1, are all within the range 27.2 to 29.5 kJ/mol. This indicates that an average value of 28.5 kJ/mol, calculated by omitting the value for the 4.26:1 solution, should adequately describe the temperature dependence of k_1 over the range studied. Figure 15 is an Arrhenius plot of the experimental data where the lines are best fit lines representing an activation energy of 28.5 kJ/mol.

The activation energy for the Li/K = 4.26 data was not used in evaluating the average value because it was determined using only three data points. There was uncertainty in the measured value of k_1 for the low temperature run, since the differences between the concentrations of consecutive samples were in the order of magnitude of the precision of analysis which could be obtained with the mass spectrometer. The value of the average activation energy calculated with the inclusion of this datum point is 29.1 kJ/mol.

The value of the common activation energy calculated in this work is the same as that determined by Rochard (3) in her work with potassium methylamide as catalyst. The results reported by Kalra and Otto (2) for an aminomethane solution containing 0.41 $\frac{\text{m mol}}{\text{g amine}}$ PMA are plotted in Figure 16, along with the data from this work for the 0.31 and 0.40 m mol/g amine PMA solutions. They obtained data over a fairly narrow temperature range and although their data for temperatures of approximately -23 and -30°C are in fair agreement with the values of k_1 measured for a 0.40 m mol/g PMA solution in this study, the values of

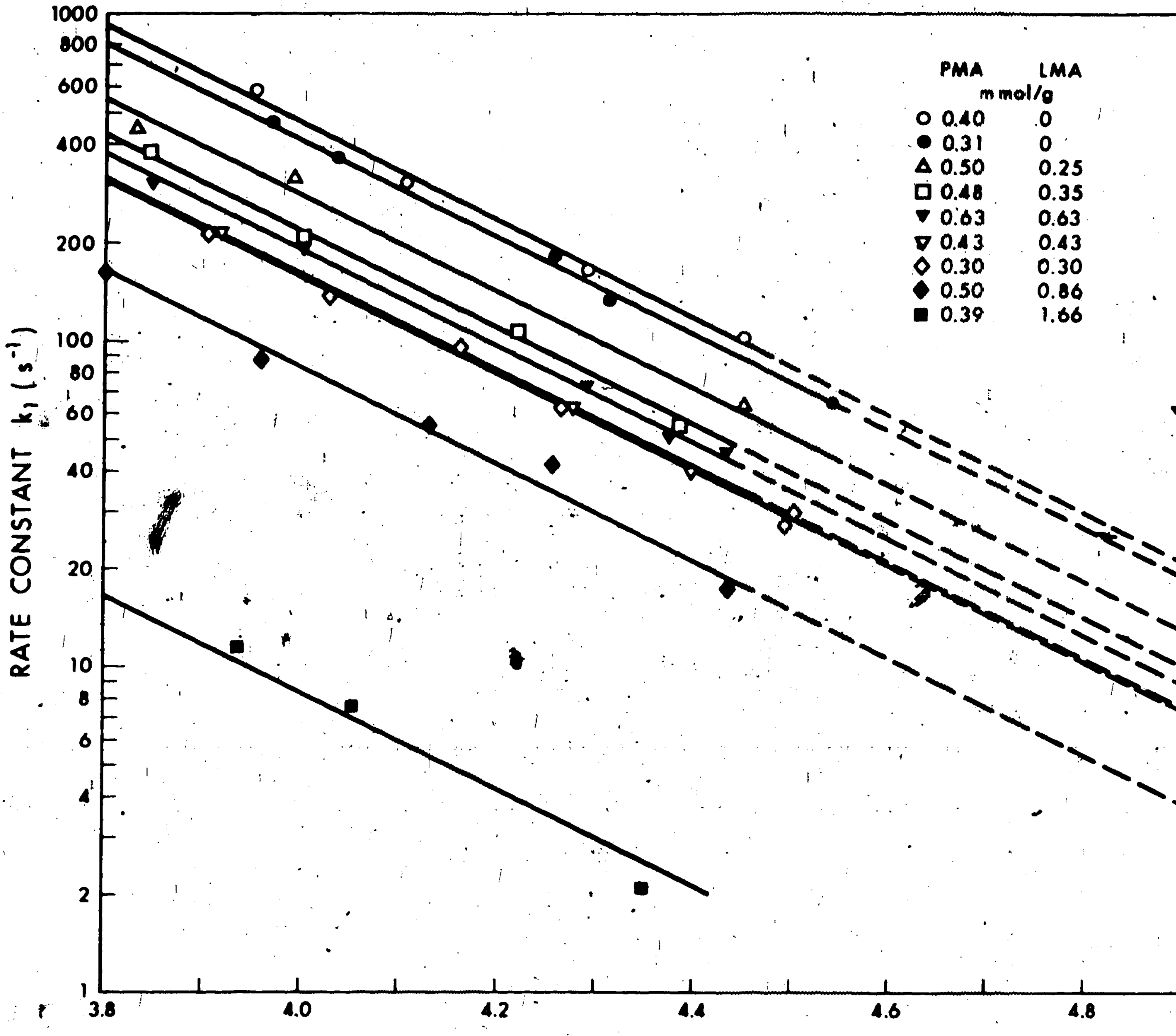

Figure 15: Experimental Data Plotted with a Common Activation Energy of 28.5 kJ/mol

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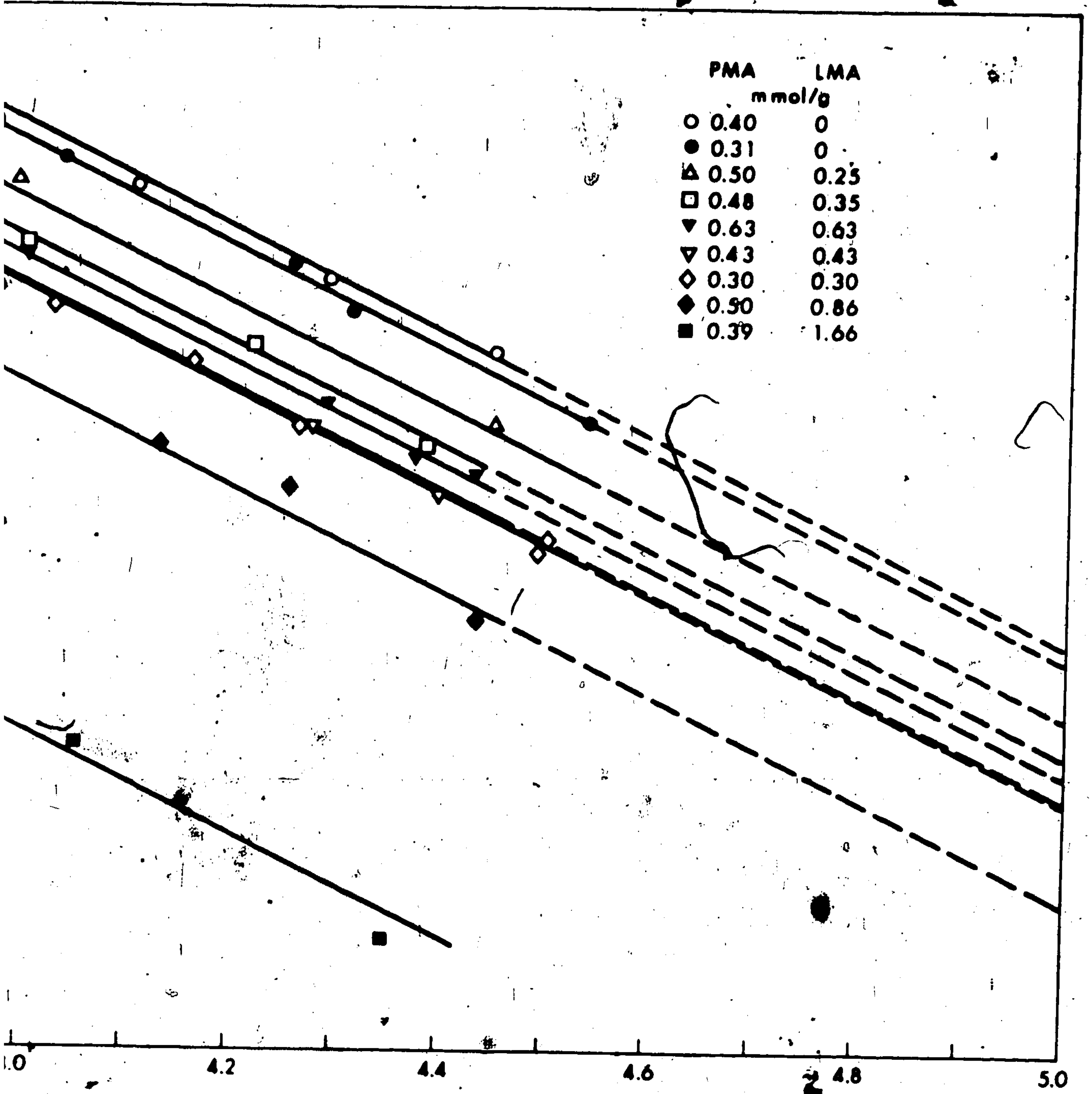

Figure 15: Experimental Data Plotted with a Common Activation Energy of 28.5 kJ/mol

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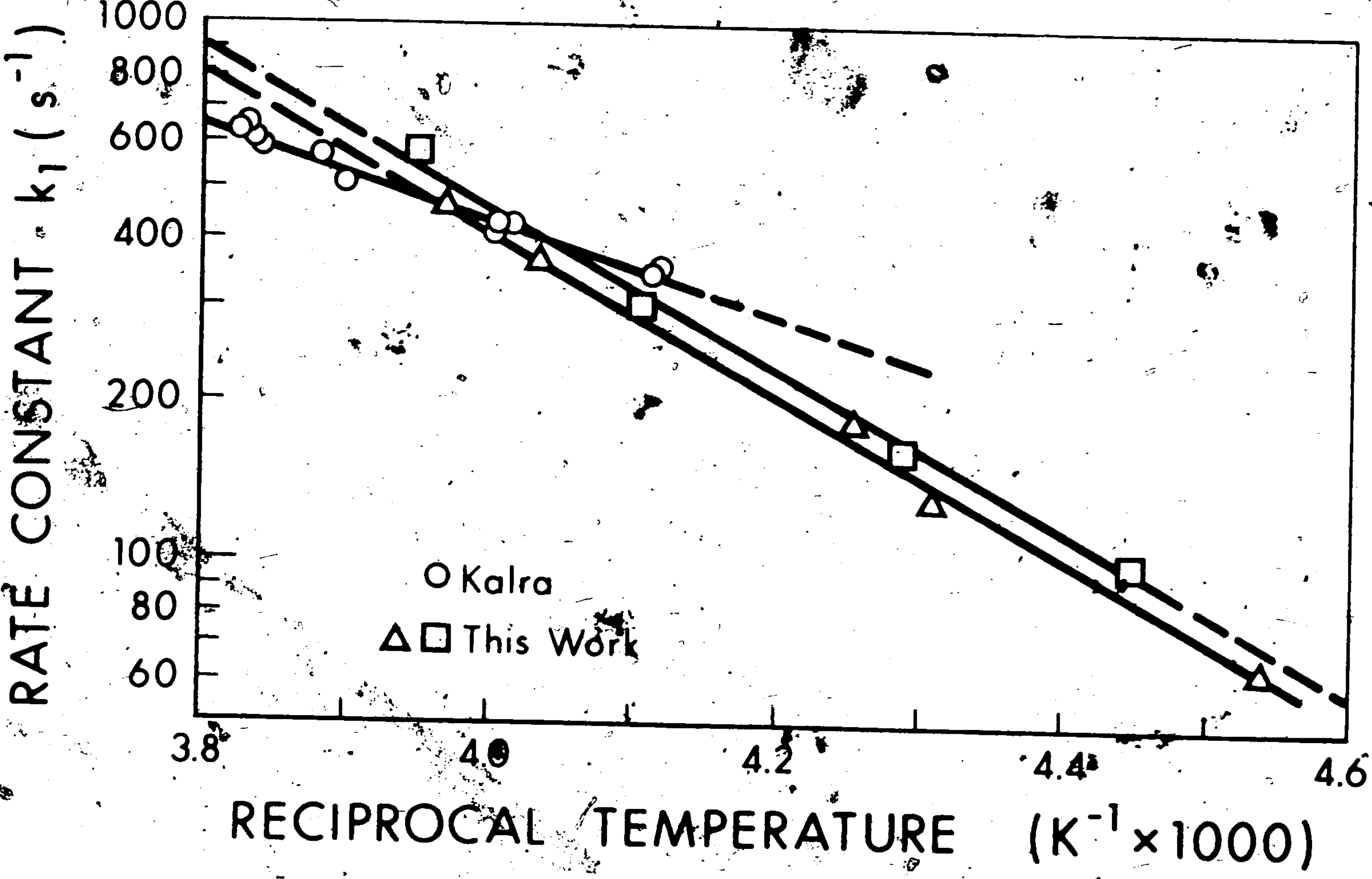

Figure 16: Arrhenius Plot Showing Data from Kalra (2) and This Work with PMA Solutions

k_1 obtained at approximately -16 and -11°C appear to be low. The activation energy calculated using their data is 16.8 kJ/mol. The reason for this low value is not clear. There is some uncertainty in the catalyst concentrations reported by Kalra and Otto. Their analysis of the amide solutions consisted of analyzing for the total potassium concentration, using atomic absorption spectroscopy, and equating this value to the PMA concentration. Thus any catalyst decomposition was not accounted for and the amide concentrations may have been lower than reported. However, due to the order in which their experiments were performed, this is not an adequate explanation for the low activation energy observed.

5.2 Effect of Potassium Methylamide Concentration on k_1

The dependence of k_1 on PMA concentration was studied by both Rochard (3) and Kalra and Otto (2). Kalra and Otto's work indicated that the rate constant is almost linearly dependent on concentration up to about 0.27 m mol/g but becomes less dependent at higher concentrations. Rochard's data for catalyst concentrations less than about 0.01 m mol/g also support a linear dependence on catalyst concentration. Her measurements were made using a stirred reactor and it appears that the mass transfer resistance became significant at higher concentrations.

The data obtained in this study for aminomethane solutions containing 0.40 and 0.31 m mol/g PMA show a dependence on concentration that is less than linear. However the 0.31 m mol/g solution contained 22.5% decomposition product and the effect of this is not well defined. These data (0.40 and 0.31 m mol/g PMA solutions) were used along with data from Kalra and Otto's and Rochard's work to prepare Figure 17, which is a plot of the effect of PMA concentration on k_1. The points

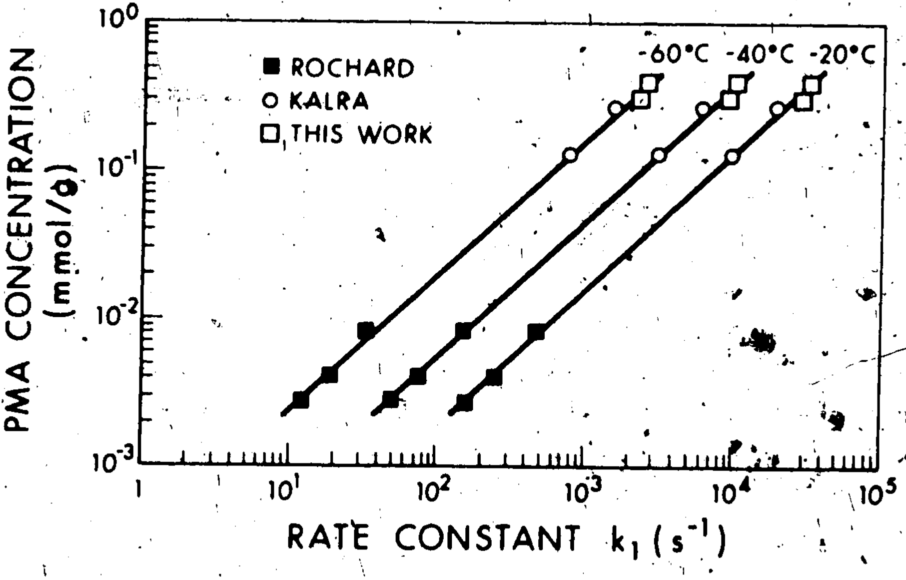

Figure 17: Variation of the Kinetic Rate Constant with PMA Concentration

TABLE 4

RATE CONSTANTS USED FOR THE DETERMINATION OF THE EFFECT OF PMA CONCENTRATION ON k_1

	Catalyst Concentration m mol/g amine	Rate Constant, k_1 (min^{-1}) -60°C	-40°C	-20°C
Rochard	2.78×10^{-3}	12.2	48.2	154
	4.09×10^{-3}	19.0	75.1	240
	8.62×10^{-3}	37.8	150	478
Kalra	0.13	774	3070	9780
	0.27	1520	6000	19200
This Work	0.31	2310	9180	29200
	0.40	2580	10300	32700

were obtained from the smoothed lines on Figure 15 and by extrapolation of Kalra and Otto's data for PMA concentrations of approximately 0.27 and 0.13 m mol/g and Rochard's data for PMA concentrations less than 0.01 m mol/g. An activation energy of 28.5 k J/mol was assumed for these extrapolations. Rochard's data were initially fit to the Arrhenius model using least squares. The points used for Figure 17 are given in Table 4. A least squares fit of these calculated points, combined with the Arrhenius equation to describe the temperature dependence, gives

$$k_1 = 1.11 \times 10^9 \, e^{-E/RT} \, C^{1.085} \tag{5.1}$$

The fact that the exponent on C is close to one indicates that the dependence of k_1 on C is linear, at least up to PMA concentrations of 0.4 m mol/g. The dependence at higher concentrations is not defined and extrapolations of k_1 to PMA concentrations above 0.4 m mol/g should be made with caution.

5.3 Exchange with PLMA Solutions

The effect of the LMA/PMA molar ratio on k_1 for a solution containing approximately 0.45 m mol/g PMA is shown on Figure 18. The addition of LMA to a solution of PMA in aminomethane results in a significant reduction in the rate of exchange with that solution. This decrease in k_1 is approximately exponential with an increasing ratio of LMA to PMA concentrations. For example, k_1 for a solution containing 0.45 m mol/g each of PMA and LMA is approximately one third that for a 0.45 m mol/g PMA solution, whereas if the LMA to PMA molar ratio is 4 the rate is reduced by a factor of about 60.

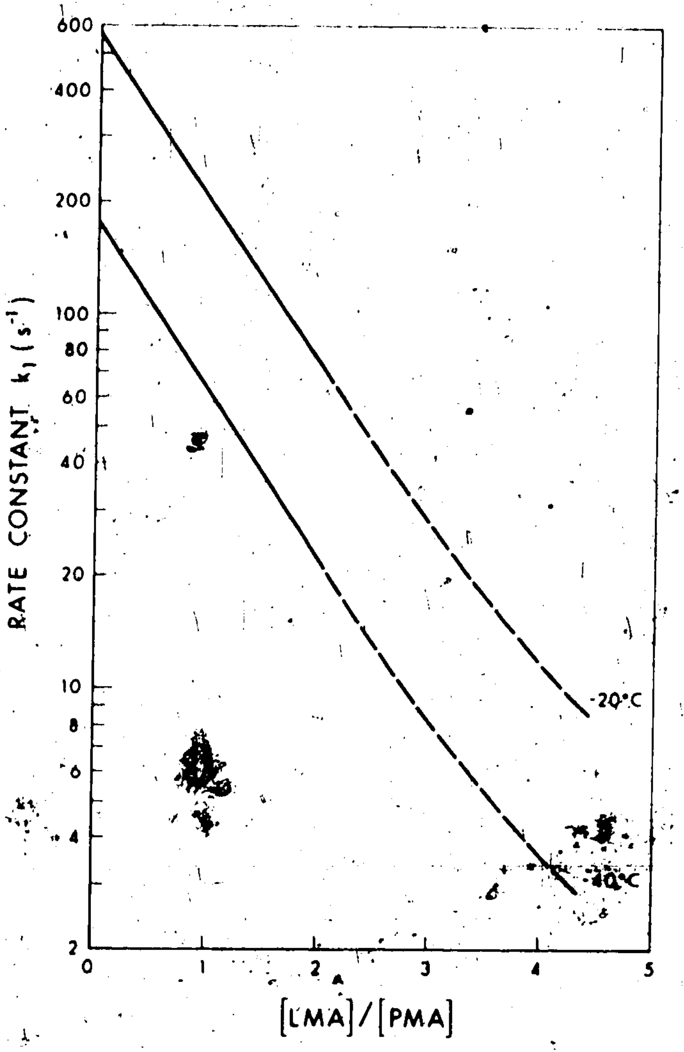

Figure 18: Effect of [LMA]/[PMA] Ratio on k_1 for a Solution Containing 0.45 m mol/g PMA

Figure 19 shows the effect of increasing amide concentration on k_1 with a constant LMA/PMA molar ratio of one. The rate does not increase linearly with PMA concentration.

Due to these observations and because of the uncertainty in the effect of PMA concentrations greater than 0.4 m mol/ℓ on k_1 for PMA solutions, the following model was selected in an attempt to fit all the experimental data to a single equation.

$$k_1 = B(1)\, e^{-E/RT} \left(1 - e^{-B(2)[PMA]^{B(3)}}\right) e^{-\left(\frac{[LMA]}{[PMA]}\right)^{B(4)}} \qquad (5.2)$$

This is an extension of the model used by Kalra and Otto (2) to fit their PMA data. A nonlinear regression algorithm, proposed by Marquardt (21), was used to evaluate the parameters in this model, yielding

$B(1) = 4.41 \times 10^{9}\ (s^{-1})$

$B(2) = 0.114$

$B(3) = 0.220$

$B(4) = 0.915$

with

$E = 28.5$ kJ/mol

The rate constant at −20°C, calculated with Equation (5.2), is shown as a function of PMA concentration on Figure 20, for LMA to PMA ratios ranging from 0.5 to 4.0.

A comparison of the measured values of k_1 with those calculated using Equation (5.2) is given in Table 5. The model overestimates k_1 for solutions containing LMA to PMA molar ratios greater than about 1.5

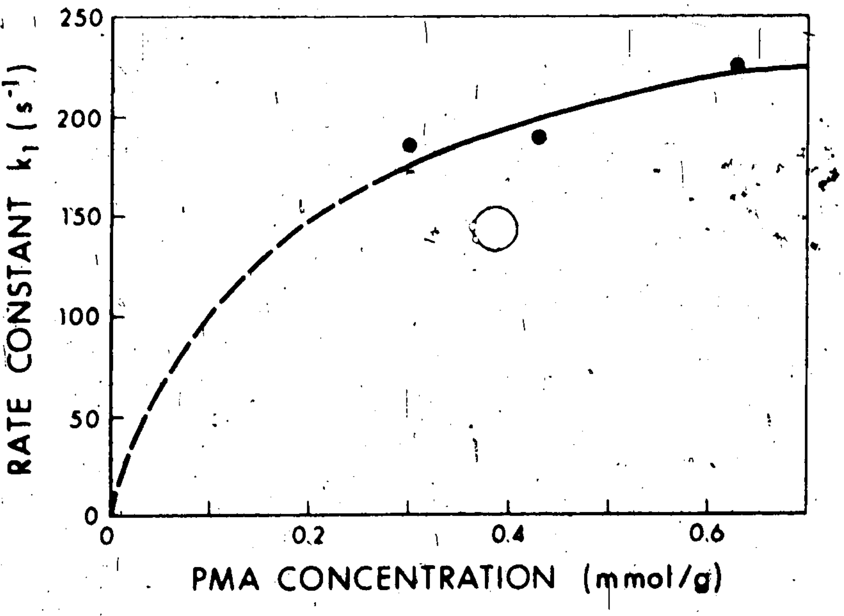

Figure 19: Effect of PMA Concentration on k_1 for a Solution Containing a [PMA]/[LMA] Ratio of 1

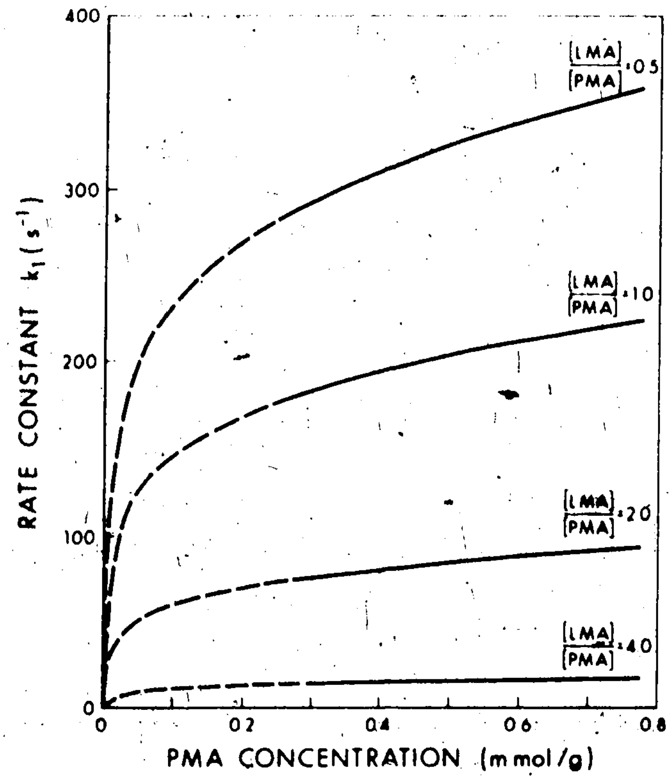

Figure 20: Variation of k_1 with PMA Concentration at -20°C for Constant Values of the [PMA]/[LMA] Ratios (Calculated with Equation (5.29))

TABLE 5

COMPARISON OF THE MEASURED AND CALCULATED RATE CONSTANTS USING EQUATION (5.2)

Concentration of PMA (m mol/g)	Concentration of LMA (m mol/g)	$\frac{[LMA]}{[PMA]}$	k_1 (measured) (s^{-1})	k_1 (calculated) (s^{-1})	$\frac{k_{1_{meas}} - k_{1_{calc}}}{k_{1_{meas}}}$
0.31	0.0	0.0	132	140	0.063
0.31	0.0	0.0	364	375	0.031
0.31	0.0	0.0	183	178	0.029
0.31	0.0	0.0	462	472	0.023
0.31	0.0	0.0	64	67	0.039
0.30	0.30	1.0	137	142	0.031
0.30	0.30	1.0	95	90	0.060
0.30	0.30	1.0	63	63	0.003
0.30	0.30	1.0	27	29	0.051
0.30	0.30	1.0	29	27	0.077
0.30	0.30	1.0	214	216	0.005
0.43	0.43	1.0	64	66	0.036
0.43	0.43	1.0	214	223	0.040
0.43	0.43	1.0	40	42	0.091
0.63	0.63	1.0	51	50	0.022
0.63	0.63	1.0	46	41	0.011
0.63	0.63	1.0	193	182	0.060

TABLE 5 (continued)

Concentration of PMA (m mol/g)	Concentration of LMA (m mol/g)	$\frac{[LMA]}{[PMA]}$	k_1 (measured) (s^{-1})	k_1 (calculated) (s^{-1})	$\frac{k_{1_{meas}} - k_{1_{calc}}}{k_{1_{meas}}}$
0.63	0.63	1.0	307	306	0.003
0.63	0.63	1.0	72	67	0.070
0.39	1.66	4.26	2	3	0.500
0.39	1.66	4.26	12	13	0.111
0.39	1.66	4.26	8	9	0.150
0.40	0.0	0.0	101	96	0.044
0.40	0.0	0.0	582	528	0.093
0.40	0.0	0.0	164	167	0.016
0.40	0.0	0.0	303	312	0.029
0.50	0.86	1.72	18	20	0.170
0.50	0.86	1.72	88	104	0.188
0.50	0.86	1.72	[illegible]	58	0.064
0.50	0.86	1.72	41	38	0.078
0.50	0.86	1.72	161	178	0.106
0.48	0.35	0.73	54	59	0.089
0.48	0.35	0.73	208	214	0.028
0.48	0.35	0.73	107	104	0.025
0.48	0.35	0.73	381	374	0.020

TABLE 5 (continued)

Concentration of PMA (m mol/g)	Concentration of LMA (m mol/g)	$\frac{[LMA]}{[PMA]}$	k_1 (measured) (s^{-1})	k_1 (calculated) (s^{-1})	$\left\lvert \frac{k_{1_{meas}} - k_{1_{calc}}}{k_{1_{meas}}} \right\rvert$
0.50	0.25	0.50	62	60	0.044
0.50	0.25	0.50	447	490	0.097
0.50	0.25	0.50	312	285	0.086

but fits all the other data to ± 10%.

5.4 Accuracy of the Data

The accuracy of the values of k_1 is highly dependent on the accuracy with which the diffusivity of HD and the solubility of hydrogen in aminomethane are known. Kalra's (12) detailed error analysis indicated that values of k_1 determined for the hydrogen-aminomethane system using the sphere absorber apparatus are accurate to ± 10%.

The equilibrium concentrations in the gas phase were estimated using an approximate mass balance and errors in these values may have resulted. Kalra (12) showed that the error introduced in the value of k_1 by an incorrect estimation of y_e increased as the concentration in the gas phase approached y_e. The experiments in this work were run for a short time in comparison to that which would be required to approach equilibrium. The lowest concentration reached in the gas phase was 61 ppm which was more than twice the equilibrium concentration. The rate constant for the run dated November 4, 1975 was calculated using values of y_e equal to 19.6 and 23.0 ppm to show the magnitude of the error introduced in a typical experiment by an incorrect estimation of y_e. The resulting values were 164 s^{-1} with $y_e = 19.6$ ppm and 167 s^{-1} with $y_e = 23.0$ ppm, indicating an error of about 2%. This is well within the estimated accuracy of the data.

6. CONCLUSIONS

The sphere absorber was used to measure rate constants for the exchange of deuterium in the Hydrogen-aminomethane system, with both PMA and PLMA catalysts. The temperature range of the investigation was -10 to -50°C. An activation energy of 28.5 kJ/mol was calculated for the reaction, which was in agreement with that determined by Rochard (3). The accuracy of the values of k_1 was estimated to be ± 10% and is dependent upon the accuracies of the diffusivity of HD in liquid aminomethane, solubility of the hydrogen and the gas analysis.

The analysis of the aminomethane, solutions for the catalyst concentrations indicated that a portion of the PMA decomposed to dimethylformamidine in some of the solutions. The effect of this compound on the rate of reaction is unknown and therefore the knowledge of its presence is important in a kinetic study. The concentrations of PMA and LMA in these solutions were assumed to be equal to the proportion of the total potassium and lithium concentrations which could be attributed to the CH_3NH^- concentration.

Analyses of the data, using Froessling's equation for forced convection around single spheres and the two film theory for resistance to mass transfer, indicated that the gas phase resistance to mass transfer was an important consideration in this work. The percentage of the resistance in the gas phase increased as the rate constant increased and accounted for as much as 5% of the total resistance.

A model was developed relating the rate constant to the PMA concentration, for a PMA concentration range of 0 to 0.4 m mol/g, shown as

$$k_1 = 1.11 \times 10^9 e^{-E/RT} C^{1.085} \qquad (5.1)$$

where E = 28.5 kJ/mol. The rate constants measured with PMA as catalyst were at least 35 times the corresponding values reported for the hydrogen-ammonia system.

An expression, shown as

$$k_L = 4.41 \times 10^9 e^{-E/RT} (1 - e^{0.114[PMA]^{0.220}}) e^{-(\frac{[LMA]}{[PMA]})^{0.915}} \qquad (5.2)$$

was developed to correlate all the data obtained in this work. The rate constant decreased almost exponentially as the LMA to PMA concentration ratio increased. A possible explanation of this phenomenon is that each lithium ion forms a complex with two amide ions resulting in a large reduction in the number of amide ions available as catalyst. Although the addition of LMA to a PMA solution resulted in a large reduction of the rate constant, its presence was considered attractive because:

1. The amide solution was more stable and less decomposition of the amide was observed in solutions which also contained LMA.
2. PLMA solutions were less reactive and the amides were less likely to precipitate, which resulted in a much safer solution to work with in comparison to PMA solutions.

The measurements of the rate constants and their dependence on temperature and catalyst concentrations may be used to predict transfer coefficients and thus tray efficiencies for the design of the cold contacting towers used in the hydrogen-aminomethane, deuterium enrichment process.

NOMENCLATURE

a_1, a_2, a_3	Constants in Equation (B.4)
a_{KNH_2}	Activity of undissociated KNH_2
$a_{NH_2^-}$	Activity of the NH_2^- ion
A	Pre-exponential factor (s^{-1})
A [illegible]	Surface area of the absorber corrected for the liquid film (cm^2)
A_J	Surface area of the laminar jet (cm^2)
A_s	Surface area of the dry sphere (cm^2)
A_T	Surface area of the sphere and jet (cm^2)
A_0, A_1, A_2	Constants [illegible] Equation (2.5)
B(1), B(2), B(3), B(4)	Parameters in Equation (5.2)
C	Concentration of PMA in aminomethane (m mol/g)
C	Concentration of solute gas in the liquid phase ($\frac{mol}{cm^3}$)
C^*	Dimensionless concentration defined by Equation (2.25)
C_e	Concentration of HD in the liquid phase in chemical equilibrium with the concentration of CH_3NHD in the bulk liquid (mol/cm^3)
C_i	Concentration of solute at the interface (mol/cm^3)
C_o	Equilibrium concentration of solute in the liquid phase (mol/cm^3)
C_{st}	Absolute deuterium concentration of the principal standard (D/D+H in ppm)
C_1^*	Absolute deuterium concentration of a hydrogen sample (D/D+H in ppm)
C_1, C_2, C_3, C_4	Constants in Equation (B.5)

d_J	Diameter of the laminar jet (cm)
d_s	Diameter of the sphere absorber (cm)
D	Molecular diffusion coefficient (cm^2/s)
D_{AB}	Molecular diffusion coefficient of specie A in specie B (cm^2/s)
D_{mix}	Diffusivity of HD in the H_2-CH_3NH_2 mixture (cm^2/s)
E	Activation energy (kJ/mol)
$f(KT/\epsilon)$	Collision function
g	Acceleration due to gravity (cm/s^2)
G	Total gas absorption rate (g/s)
G_i	Instantaneous absorption rate (mol/s)
h	Planck's constant (erg-s)
H	Henry's law coefficient (atm/mole fraction)
I_2	Current signal corresponding to the H_2 concentration in the gas sample (Amperes)
I_3	Current signal corresponding to the HD concentration in the gas sample (Amperes)
k_c	Mass transfer coefficient ($\frac{mol}{s\ cm^2\ mol/cm^3}$)
k_G	Gas phase transfer coefficient ($\frac{mol}{cm^2\ s\ kPa}$)
k_{KNH_2}	Specific rate constant for catalysis by undissociated KNH_2, Equations (2.2) and (2.3) (s^{-1})
k_L	Liquid phase transfer coefficient (cm/s)
$k_{NH_2^-}$	Specific rate constant for catalysis by the NH_2^- ion, Equations (2.2) and (2.3) (s^{-1})
k^*	Slope of the $\ln(\frac{y - y_e}{y_{in} - y_e})$ vs t curve (s^{-1})
k_o	Specific rate constant for catalysis by the NH_2^- ion (s^{-1})

k_1	Pseudo first order rate constant for the forward reaction (s^{-1})
k_2	Pseudo first order rate constant for the reverse reaction (s^{-1})
k	Boltzmann's constant (erg/K)
K_{eq}	Chemical equilibrium constant
K_L	Overall mass transfer coefficient (cm/s)
ℓ	Length of the laminar jet (cm)
L	Volumetric flowrate (cm^3/s)
m	Molecular mass, Equation (2.6)
m*	Number of exchangeable hydrogen atoms in a hydrogen molecule
M	Dimensionless rate constant defined by Equation (2[illegible])
M_A, M_B	Molecular weights of A and B, respectively
n_{H_2}	Total number of moles of H_2 gas
n*	Number of exchangeable hydrogen atoms in an aminomethane molecule
N	Avogadro's number
P_{HD}	Partial pressure of HD (kPa)
P_{H_2}	Partial pressure of H_2 (kPa)
P_t	Absolute pressure (kPa)
r_{AB}	Molecular separation at collision (Å)
R	Radius of the sphere absorber (cm)
R_e	Gas phase Reynolds number $(\frac{2\ R\ v_{av}\ \rho_G}{\mu})$
R_g	Universal gas constant $(8315\ \frac{cm^3\ kPa}{mol\ \ K})$
R_{st}	Ratio of mass three (HD) to mass two (H_2) currents (I_3/I_2) for the principal standard.
R*	Ratio of mass three (HD) to mass two (H_2) currents

[illegible]	(I_3/I_2) for a sample
t	Time (s)
t_{max}	Time of exposure of a surface element of liquid on the sphere absorber (s).
T	Absolute temperature (K)
T_c	Critical temperature (K)
T_r	Reduced temperature
v_{av}	Average velocity of the gas in the absorption chamber (cm/s)
v_o	Liquid velocity at the film surface (cm/s)
v_ψ	Liquid velocity along a streamline (cm/s)
V	Total volume of the system occupied by gas (cm^3)
V_A	Volume of the saturator which contained liquid aminomethane (cm^3)
V_C	Critical volume (cm^3/mol)
V_T	Total volume of the system containing gas pl[illegible] portion of the saturator which contained liquid (cm^3)
V_2	Molar volume of solute, Equation (2.6) $(\frac{cm^3}{mol})$
x	Coordinate measured from the film surface in a negative radial direction (cm)
x	Mole fraction of HD in the liquid phase
x_e	Mole fraction of HD in the liquid phase in chemical equilibrium with the CH_3NHD concentration in the bulk liquid
y	Coordinate which accounts for the stretching of the liquid film $(\frac{x}{\Delta})$
y	$[HD]/([HD] + [H_2])$
y_e	Mole fraction of HD in the gas phase in equilibrium

	with the CH_3NHD concentration in the liquid phase
y_{in}	Mole fraction of HD in the gas phase at t = 0
y^*	Mole fraction of HD in the gas phase
α	Separation factor between D and H between aminomethane and hydrogen
α_N	Relative volatility of CH_3NHD and CH_3NH_2
α_1	Property of the solute, Equation ([illegible]) = $\sigma/[\frac{V_2}{N}]^{1/3}$
β	1000/T (K^{-1})
δ_{DI}	Dimensionless ratio of gas concentrations ($\frac{HD}{H_2}$) defined by Equation (3.3)
δ_{st}	Dimensionless ratio of standard concentrations ($\frac{[illegible]}{H_2}$) defined by Equation (3.4)
Δ	Thickness of the liquid film (cm)
Δ_1	Thickness of the liquid film at the sphere equator (cm)
ϵ_{AB}	Energy of molecular interaction (erg)
ϵ	Collision energy of solute molecule, Equation (2.6) ($\frac{g\ cm^2}{s^2}$)
θ	Angle measured from the top of the sphere absorber (rad)
Λ^*	Quantum parameter, Equation (2.6) = $h/\sigma(m\epsilon)^{1/2}$
μ	Viscosity (g/cm s)
μ_1	Viscosity of the solvent, Equation (2.6) (cp)
ν	Kinematic viscosity (cm^2/s)
ρ_L	Molar density of the liquid phase ($\frac{mol}{cm^3}$)
ρ_G	Density of the gas (g/cm^3)
σ	Collision diameter of solute molecules, Equation (2.6) (Å)

ψ	Variable defined by Equation (2.23)
ψ_2	Maximum value of ψ, occurring at $\theta = \pi$ for a spherical film

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APPENDIX A

DETAILED OPERATING PROCEDURES

A.1 The Exchange Experiment

The following procedure was used to conduct a hydrogen-aminomethane exchange experiment.

1) Start the two auxiliary refrigeration units and cool the feed and receiving tanks.
2) Open the distributor solenoid valve and evacuate the entire exchange apparatus, between the liquid inlet and return valves, to less than 5 μ.
3) Fill the exchange apparatus with ultra high purity hydrogen to a pressure of about 25 cm Hg (gauge). The system should be checked for leaks by observing the manometer over a period of at least two hours.
4) Providing there are no leaks, the exchange apparatus may be refrigerated in the following manner.
    a) Replace the door on the front of the refrigerated air bath.
    b) Start the circulation fan located inside the air bath.
    c) Turn on the power to the temperature recorder so that the suction and discharge temperatures in the "York" refrigeration unit can be monitored.
    d) Start the "York" refrigeration unit.
    e) Adjust the setting on the power transformer which controls the heater in the air bath to obtain the desired temperature. The apparatus should be left overnight since it takes about ten hours for a steady temperature to be reached.

5) Remove the hydrogen contained in the receiving tanks with the vacuum pump. The pressure in these tanks at the beginning of an experimental run should be approximately 5 psia.

6) Start the refrigerated methanol circulation pumps which supply the coolant to the double pipe heat exchangers located on the feed and return lines. This ensures that these lines will be cold throughout the run.

7) Evacuate the exchange apparatus and then fill the system with enriched hydrogen to a pressure of about 25 cm Hg (gauge).

8) Introduce some dry aminomethane into the saturator from the storage tank and start the hydrogen circulation pump. The gas rotameter should read between [illegible] to 20 percent of full scale.

9) Use the cathetometer to measure the distance from the jet nozzle to the top of the sphere. [illegible] a distance on the take off tube 1.25 cm below the bottom [illegible] leave the cathetometer in this position. The liquid level in the take off tube will eventually be maintained at this height.

10) Start the vacuum pump connected to the gas sampling apparatus ~~and~~ evacuate the entire sampling system. Close the stopcock (9) (Fig. 4) so that the absolute pressure is indicated on the manometer.

11) Surround the cold traps on the gas sampling system with liquid nitrogen and prepare to take the first sample as described in step (23).

12) Turn on the power to the potentiometer and set the zero. Record the readings of the thermocouples located in the liquid and gas lines above and below the absorption chamber.

13) Open the valves connecting the ultra high purity hydrogen cylinder

to the feed tanks and raise the pressure in the tanks to about 40 psig. All the valves on the feed line except the "Whitey" control valve and the bypass valve should be opened.

14) Open all valves on the liquid return line except the ball valve.

15) Close the distributor solenoid valve.

16) The system is now ready for the introduction of the liquid feed. Open the bypass valve on the feed line about half a turn. A[illegible] as the liquid enters the liquid rotameter, close this valve. Open the "Whitey" control valve about 2 1/2 turns. This procedure aids in the prevention of solid plugs in the control valve during start up.

17) The desired liquid level in the entrained hydrogen removal section must now be set. This is accomplished by opening the valve connecting the top of this section to the atmosphere and allowing the liquid level to rise. Care must be taken to maintain a liquid seal on the inlet to the distributor, to prevent the hydrogen contained in the remainder of the apparatus from escaping. Once the desired level is reached close the valve and open the distributor solenoid valve.

18) The liquid level will now rise in the distributor and enter the jet nozzle approach tube. As soon as the liquid wets the sphere the timer should be started. Adjust the "Whitey" control valve so that the liquid rotameter reads between 70 and 80 percent of full scale. This corresponds to a liquid flowrate of approximately 0.275 cc/sec.

19) The liquid in the take off tube should be drained to the return tanks when the level reaches about half way up the tube. This can

be accomplished by opening the ball valve located on the liquid return line. The liquid should be drained three or four times in this manner to prevent solid plugs from forming in the metering valve.

20) The liquid return bypass valve may now be closed and the liquid level in the take off tube adjusted to the proper height with the metering valve.

21) Close the distributor solenoid valve when the liquid level in the distributor rises to about two inches above the top of the liquid approach tube.

22) Maintain the liquid flowrate and the liquid level in the take off tube at the proper values by adjusting the respective control valves.

23) The first gas sample can be taken at approximately 400 seconds after the clock was started, in the following manner. All numbers in parentheses refer to equipment locations on Figure 4.

a) At least 300 seconds before the sample time attach a sample bomb to the ground glass joint (7).

b) Evacuate both the valve side and the sample side of the sample bomb. Close the stopcock on the sample bomb.

c) About 50 seconds before the desired sample time, close the vacuum valve (2) and the stopcock (4). Open the sample valve (1) and allow a sample into the sample volume (3).

d) Close the sample valve and discard the sample by opening the vacuum valve. This procedure flushes the sample lines so that a true sample is obtained at the desired sampling time.

e) Close the vacuum valve after the sample is completely pumped out.

f) Open the sample valve (1) when the clock indicates the desired sampling time. Allow sufficient time for the sample to enter the sample volume, about 3 seconds, and then close the valve.

g) Open stopcock (4). The sample pressure will be indicated on the manometer (11).

h). Open and then close the stopcock on the sample bomb. A decrease in the pressure should be noted on the manometer as the sample enters the bomb. Close stopcock (6) and remove the sample bomb.

i) Evacuate the system by opening valve (2), and attach the next sample bomb.

j) The readings from the thermocouples described in step (10), the liquid and gas rotameter readings and the system pressure should be recorded after each sample is withdrawn.

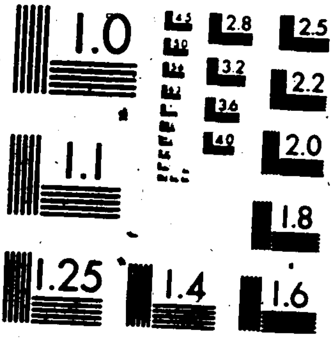
24) Take samples, as described in step (23), at intervals of 600 to 1000 seconds until a sufficient number are available. A minimum of eight samples should be taken for each experimental run.

25) After the last sample has been taken close the shut off valve on the feed line. Close the liquid feed line on the feed tanks and open the corresponding valve on the return tanks. Open the shut off valve on the feed line and allow the liquid in the distributor and dissolved hydrogen removal section ~~to~~ drain back to the return tanks. Close the feed line shut off valve.

26) Drain the liquid remaining in the take off tube and the return line and then close the ball valve on the return line.

27) Measure the distance from the top of the saturator to the liquid aminomethane level. Immerse the dry amine storage tank in liquid

2 OF/DE 2



MICROCOPY RESOLUTION TEST CHART
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nitrogen and open the saturator solenoid valve. Allow the amine to return to the storage tank and then close the solenoid valve.

28) Turn off the power to the hydrogen circulation pump, the circulating fan, the air bath heater and the methanol circulation pumps. Switch off the discharge solenoid valve on the "York" refrigeration unit and wait two or three minutes. Turn off the refrigeration unit.

29) Open the pressure relief valve on the exchange apparatus.

30) Remove the liquid nitrogen Dewar flasks from the cold traps on the sampling system and pump out the condensed amine.

31) Close the valve connecting the hydrogen cylinder to the liquid feed tanks.

32) Allow sufficient time for the exchange apparatus to return to room temperature. This will generally take until the next day.

33) Remove the door from the refrigerated air bath. Take apart the "Swagelok" fitting nearest the liquid return shut off valve, to allow the wash alcohol to drain out.

34) Open the methanol wash valve on the feed line and pump alcohol through the system. When the system is clean turn off the pump and drain as much alcohol as possible to the dump tank.

35) Fasten the "Swagelok" fitting and close the methanol wash valve. Evacuate the system to remove the remaining alcohol.

A.2 Catalyst Solution Make-Up

Potassium and lithium react violently with air or water, consequently caution must be exercised when working with these metals. The following procedure was used to make up the catalyst solutions.

1) The aminomethane used in this study, purchased from Matheson of Canada Ltd., contained a maximum of 0.8 weight percent water. This water is removed by contacting the amine with an excess of lithium in the following manner:

   a) Evacuate a clean make-up tank, shown in Figure 5. Fill the tank with argon to a pressure of about 5 psig. This provides an inert, heavier than air, atmosphere [illegible] the introduction of the lithium.

   b) Calculate the minimum amount of lithium required to completely remove all the water from the amount of amine to be dried.

   c) The lithium is obtained from A.D. MacKay Inc. in stick form. Although stored under paraffin oil it is generally coated with an oxide layer. Scrape this layer off a small excess of lithium under oil, so that a clean, shiny surface is exposed.

   d) Cut the sticks into approximately half inch lengths to provide a larger surface area for the subsequent reaction with the water.

   e) Wash off the paraffin oil with normal pentane and put the lithium pieces in the tank.

   f) Evacuate the tank to remove the argon and pentane.

   g) Connect the vapor line of the tank to the aminomethane cylinder and evacuate the connecting line.

   h) Immerse the tank in liquid nitrogen and open the valves connecting it with the amine cylinder. The amine will distill into the make-up tank by virtue of the temperature difference. The amount of amine transferred may be determined by weighing the aminomethane cylinder before and after the distillation.

   i) The reaction of the lithium with the water and the aminomethane produces hydrogen, resulting in an increasing pressure in the tank. A relief valve, set to relieve at about 80 psig, is connected to the tank to provide protection against a possible rupture due to excessive pressure. Whenever the pressure in the tank is greater than atmospheric, open the valves connecting the tank to the relief valve.

j) Periodically bleed the pressure off the tank to about 40 psig. The reaction can be considered to have gone to completion when no further pressure increase is observed.

2) The aminomethane is now dry and ready for use in a catalyst solution.

3) Calculate the amount of potassium and lithium required for the desired solution. Follow the procedure described in step (1) to prepare the solution, using the dried amine. The potassium is cleaned and cut in the same manner as the lithium.

4) Evacuate and refrigerate the feed tanks. The catalyst solution may be transferred into the feed tanks, through the dip tube on the make-up tank, under the vapor pressure of the amine.

APPENDIX B

SAMPLE CALCULATION

The values of the rate constants, k_1 (sec^{-1}), were calculated from the experimental data in the following manner. The experiment conducted on October 1, 1975 is used in this calculation.

B-1 Calculation of the Absolute Concentrations of the Gas Samples

The experimental measurements are listed in Table B-1. Columns 1 and 2 contain the sample times and the sample bomb numbers, respectively. The liquid flowrate (column 3) was recorded as the actual rotameter reading. Readings from two thermocouples (columns 4 and 5) were recorded. The temperature of the gas leaving the absorber was measured with thermocouple 15. Thermocouple 13 was employed to measure the temperature of the liquid entering the absorber, which was subsequently used as the system temperature. The system pressure, recorded in column 6, was used in the estimation of the diffusivity of HD in the gas phase. The initial pressure was used in this calculation. Column 7 contains the ratios of the HD to H_2 signals (R^*) of the gas samples, measured on the mass spectrometer, at a constant value of the mass two current of 2.4×10^{-9} amperes.

Four standards, with known deuterium concentrations, were analyzed with the gas samples to provide a calibration curve for the mass spectrometer. The measured and absolute values of these standards are given in Table B-2. The 471 ppm standard was not analyzed after the samples, for this particular experiment.

The analysis of the standards was converted in the following manner.

TABLE B-1

KINETIC EXPERIMENT DATA SHEET

Date:	1/10/75	Barometric Pressure:	70.5 cm Hg
Jet Length:	0.340 cm	Barometric Temperature:	20.0°C
Take-off Height:	1.25 cm		

Time (s)	Sample Bomb Number	Liquid Rotameter Reading	Thermocouples (m.v.) 13	Thermocouples (m.v.) 15	System Pressure (cm Hg)	R* x 10^6
0			-0.779	-0.780		
400	16	6.8	-0.770	-0.771	95.0	423.0
1000	38	6.8	-0.766	-0.767	92.8	361.4
1700	56	6.7	-0.759	-0.757	90.8	287.7
2420	50	6.9	-0.758	-0.759	88.8	238.8
3100	47	6.9	-0.757	-0.756	86.8	198.3
3900	37	7.0	-0.753	-0.752	85.4	154.1
4700	109	6.9	-0.752	-0.750	83.6	120.4
5600	3	7.0	-0.756	-0.746	82.4	85.5
6300	40 ✓		-0.756	-0.747	80.4	71.8

TABLE B-2

MASS SPECTROMETER ANALYSIS OF THE GAS STANDARDS

	$R^* \times 10^6$	D/H Absolute (ppm)
Before	-48.3	1.5
	71.2	99
	318.8	365
	434.1	471
After	-48.8	1.5
	69.2	99
	315.1	365

TABLE B-3

CONVERTED FORM OF THE GAS STANDARD ANALYSIS

	δ_{DI}	δ_{st}
Before	-1152.0	-995.9
	-777.0	-728.8
	0.0	0.0
	362.0	290.4
After	-1155.0	-995.9
	-780.0	-728.8
	0.0	0.0
	378.0	290.4

$$\delta_{DI} = (\frac{R^*}{R_{st}} - 1)\,1000 \qquad (3.3)$$

$$\delta_{st} = (\frac{C_1^*}{C_{st}} - 1)\,1000 \qquad (3.4)$$

where the terms in the above equations have been defined in Chapter 3. The 365 ppm standard was chosen as the principal standard so that R_{st} = 318.8 and 315.1 and C_{st} = 365 ppm. Table B-3 lists the results of the above calculations, which were fit to a linear equation using the least square method. The resulting calibration equation is of the form

$$\delta_{DI} = B_1 + B_2\delta_{st} \qquad (B.1)$$

where B_1 = 23.86

B_2 = 1.16

The measured R* values of the samples were converted to their corresponding δ_{DI} values, using Equation (3.3), with an average value of R_{st} given by

$$R_{st}\ (\text{mean}) = \frac{318.8 + 315.1}{2} = 317.0$$

Equation (3.4) was then used to determine the values of δ_{st} for the samples, from which the absolute concentrations were calculated with Equation (B.1). The initial sample was taken 400 seconds after the amine solution entered the absorber, to allow sufficient time for the system to stabilize. Consequently the time axis was shifted 400 seconds so that the time at which the first sample was withdrawn coincided with t=0. The corrected times and the absolute concentrations of the hydrogen samples are given in Table B-4 and plotted on Figure B-1.

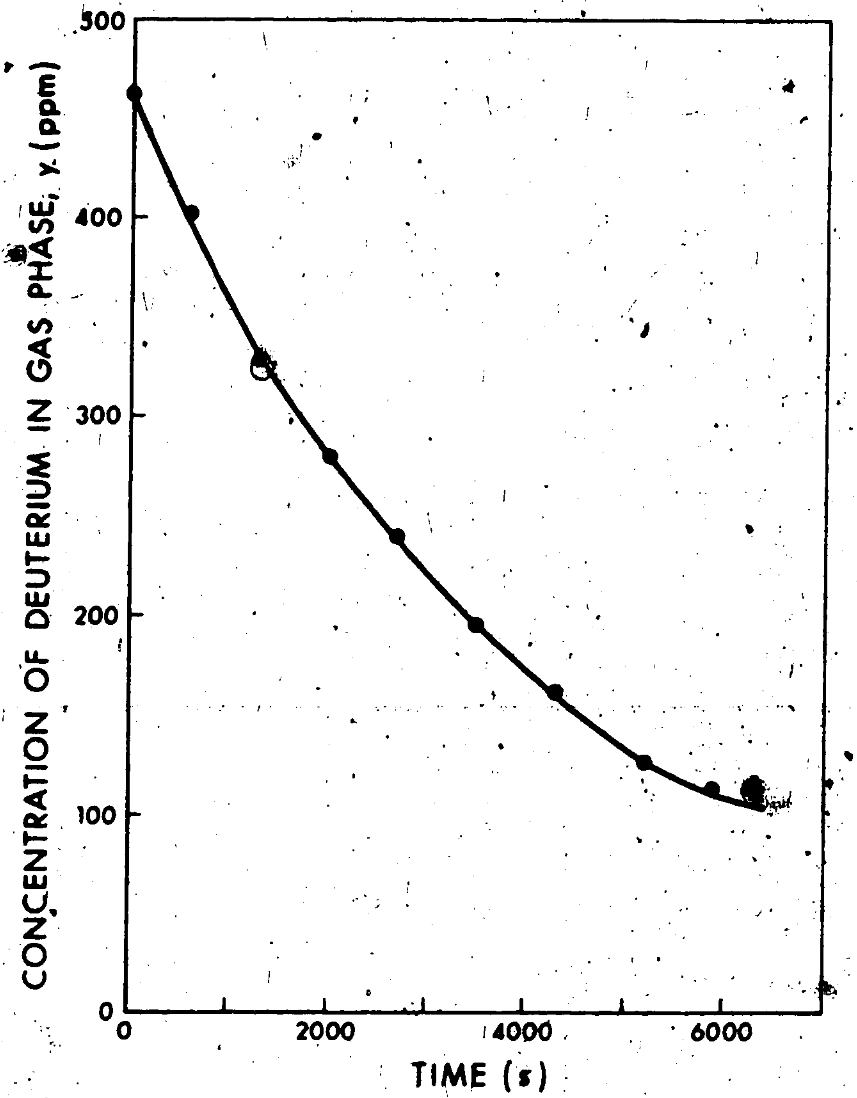

Figure B-1: Concentration of Deuterium in Hydrogen vs Time

B-2 Estimation of the Overall Liquid Phase Transfer Coefficient (K_L)

An approximate mass balance indicated that the concentration of deuterium in the amine increased by about 1 ppm dur[illegible]n experimental run. The equilibrium concentration of the hydrogen in contact with the aminomethane, at -28.5°C, measured after the subsequent experiment, was 22 ppm. The separation factor (α), defined as

$$\alpha = \frac{x_e}{y_e} \qquad (B.2)$$

where x_e = equilibrium concentration of deuterium in the aminomethane (ppm)

y_e = equilibrium concentration in the hydrogen (ppm)

at -28.5°C is 5.37, indicating an equilibrium concentration in the liquid phase of 118.2 ppm. Consequently the value of x_e used in this calculation was 117.2 ppm. The system temperature, found by linear interpolation of the copper-constantan thermocouple tables for an average reading of -0.758 mv, was -20.1°C. The corresponding separation factor is 4.97. From Equation (B.2)

$$y_e = \frac{117.2}{4.97} = 23.6 \text{ ppm}$$

This value of y_e was then used to calculate the values of $\ln\left(\frac{y - y_e}{y_{in} - y_e}\right)$. These values are given in Table B-5 and plotted on Figure B-2. y_{in} is the deuterium concentration in the hydrogen at $t = 0$.

The slope ($-k^*$) of the least squares line through the points of $\ln\left(\frac{y - y_e}{y_{in} - y_e}\right)$ vs t is

$$-k^* = \frac{-K_L A_T \rho_L R_g T}{HV} \qquad (B.3)$$

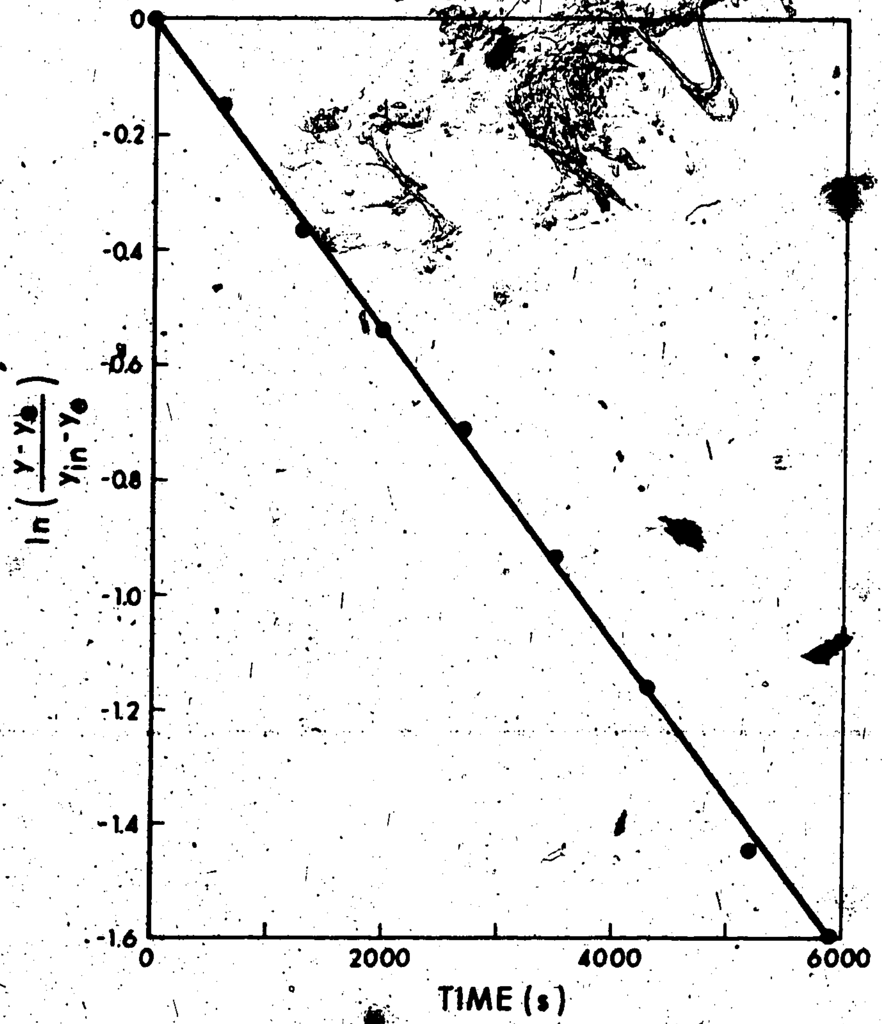

Figure B-2: Cumulative Depletion of Hydrogen vs Time

TABLE B-4

VALUES OF THE ABSOLUTE D/H CONCENTRATION VS TIME

t (s)	y (ppm)
0	463
600	402
1300	328
2020	280
2700	239
3500	195
4300	162
5200	127
5900	113

TABLE B-5

VALUES OF CUMULATIVE DEPLETION VS TIME

t (s)	$\ln \left(\frac{y - y_e}{y_{in} - y_e} \right)$
0	0.0
600	-0.1504
1300	-0.3664
2020	-0.5406
2700	-0.7122
3500	-0.9407
4300	-1.1585
5200	-1.4489
5900	-1.5908

where the symbols of Equation (B.3) have been defined in Chapter 3. The value of $-k^*$ for this calculation is $2.75 \times 10^{-[illegible]}\ s^{-1}$.

Calculation of the Interfacial Area

Sphere diameter = 3.81 cm

Jet diameter = 0.046 cm

Jet length = 0.34 cm

Liquid film thickness at the sphere equator = 0.0065 cm

Area of dry sphere = $\pi d_s^2 = \pi(3.81)^2 = 45.6\ cm^2$

The area of the sphere corrected for the film thickness with Equation (3.6) was

$$A_S = 45.6\left(1 + \frac{2.58(0.0065)}{1.905}\right)$$

$$= 46.00\ cm^2$$

Calculation of the area of the jet yielded

$$A_J = \pi d_J \ell = \pi(0.046)(0.34)$$

$$= 0.049\ cm^2$$

The total interfacial area, using Equation (3.7) was

$$A_T = 46.00 + 0.049 = 46.05\ cm^2$$

Density of the Aminomethane

The liquid density (ρ_L) was calculated with a correlation developed by Moore (11), shown as

$$\rho_L = a_1 + a_2 T + a_3 T^2 \qquad (B.4)$$

where $a_1 = 0.9058$

a_2 = -4.0095 x 10^{-4}

[illegible] = -1.[illegible]577 x 10^{-6}

T = temperature (°K)

Therefore,

$$\rho_{[illegible]} = 0.9058 - 4.0095 \times 10^{-4}(253.1) - 1.4577 \times 10^{-6}(253.1)^2$$

$$= 0.7110 \text{ g/cc}$$

Henry's Law Coefficient

The value of the Henry's law coefficient calculated with Equation (2.5) was

$$\ln H = 4.1403 + 1.66[illegible](\frac{1000}{253.1}) - 0.1160(\frac{1000}{253.1})^2$$

or

$$H = 7290 \frac{\text{atm}}{\text{mole fraction}}$$

Volume of the System Occupied by Gas

The system gas volume (V_T), including the saturator, was measured by Kalra (12) to be 256[illegible]8 cc. The volume of liquid aminomethane contained in the saturator (V_A) was subtracted from this figure to obtain the volume of the system actually filled with gas, in the following manner.

Cross sectional area of saturator = 5.344 cm^2

Length of saturator = 20.32 cm

Portion of saturator occupied by gas = 12.9[illegible] cm

Therefore

$$V_A = 5.344(20.32 - 12.91)$$

$$= 39.6 \text{ cc}$$

and

$$V = V_T - V_A = 2564.8 - 39.6$$

$$= 2525.2 \text{ cc}$$

where V = volume of the system occupied by gas (cc)

The system properties evaluated above may be substituted into Equation (B.3) to yield a value of the overall liquid phase transfer coefficient, as follows

$$K_L = \frac{k^*HV}{A_T \rho_L R_g T} \quad \frac{\text{atm cm}^3 \text{ cm}^3 \text{ °K g-mole}}{\text{s mole fraction cm}^2 \text{ g cm}^3 \text{ °K}}$$

$$= \frac{(2.73 \times 10^{-4})(7290)(2525.2)(31.1)}{(46.05)(0.7110)(82.06)(253.1)} \frac{\text{cm}}{\text{s}}$$

$$= 0.2298 \frac{\text{cm}}{\text{s}}$$

B-3 Estimation of the Gas Phase Resistance to Mass Transfer

An estimation of the gas phase mass transfer coefficient was obtained with Equation (3.16). The liquid phase transfer coefficient was then calculated with Equation (3.13).

Diffusivity of HD in the Gas Phase

The diffusivity of HD in the gas phase was estimated with the

Wilke-Lee modification of the Hirschfelder-Bird-Spotz method, Equation (3.14), as illustrated below.

1. Estimation of the Diffusivity of HD in Pure CH_3NH_2

Molecular weight of CH_3NH_2 ($M_{CH_3NH_2}$) = 31.1

Molecular weight of HD (M_{HD}) = 3.0

T = 253.1°K

P_t = 2.14 atm

$r_{CH_3NH_2\text{-}HD}$ = 3.554 Å

$K/\varepsilon_{CH_3NH_2}$ = 2.998×10^{-3}

K/ε_{HD} = 2.525×10^{-2}

$$\frac{KT}{\varepsilon_{CH_3NH_2\text{-}HD}} = \sqrt{\left(\frac{KT}{\varepsilon_{CH_3NH_2}}\right)\left(\frac{KT}{\varepsilon_{HD}}\right)}$$

$$= \sqrt{(2.998 \times 10^{-3} \times 253.1)(2.525 \times 10^{-2} \times 253.1)}$$

$$= 2.202$$

The collision function $(F(\frac{KT}{\varepsilon}))$ was estimated using Figure 2.5 in reference (22). The value obtained was 0.524. The diffusivity calculated was

$$D_{CH_3NH_2\text{-}HD} = \frac{\left(0.00107 - 0.000246\sqrt{\frac{1}{31.1} + \frac{1}{3.0}}\right)(253.1)^{3/2}\sqrt{\frac{1}{31.1} + \frac{1}{3.0}}}{(2.14)(3.554)^2(0.524)}$$

$$= 0.158\ \frac{cm^2}{s}$$

2. Estimation of the Diffusivity of HD in Pure H_2

Molecular weight of H_2 = 2.0

$r_{H_2\text{-HD}}$ = 2.963 Å

K/ε_{H_2} = 3.003×10^{-2}

$$\frac{KT}{\varepsilon_{H_2\text{-HD}}} = \sqrt{(3.003 \times 10^{-2})(253.1)(2.525 \times 10^{-2})(253.1)}$$

$$= 6.97$$

and $F(\frac{KT}{\varepsilon}) = 0.397$.

Substitution in Equation (3.14), yielded

$$D_{H_2\text{-HD}} = \frac{(0.00107 - 0.000246\sqrt{\frac{1}{3} + \frac{1}{2}})(253.1)^{3/2}\sqrt{\frac{1}{3} + \frac{1}{2}}}{(2.14)(2.963)^2(0.397)}$$

$$= 0.416\ \frac{cm^2}{s}$$

3. Estimation of the Diffusivity of HD in the Mixture

The following equation was used to calculate the vapor pressure of the aminomethane at the temperature of the system.

$$\ln P_{CH_3NH_2} = C_1 + \frac{C_2}{T} + C_3T + C_4 \ln T \qquad (B.5)$$

where C_1 = 100.906

C_2 = -5716.32

C_3 = 0.02248

C_4 = -15.3

$P_{CH_3NH_2}$ = vapor pressure of CH_3NH_2 (atm)

Therefore

$$\ln P_{CH_3NH_2} = 100.906 - \frac{5716.32}{253.1} + 0.02248(253.1) - 15.3 \ln (253.1)$$

$$= -0.6597$$

or

$$P_{CH_3NH_2} = 0.517 \text{ atm}$$

The mole fractions aminomethane and hydrogen in the gas phase were calculated as

$$y_{CH_3NH_2} = \frac{P_{CH_3NH_2}}{P_T} = \frac{0.517}{2.14} = 0.242$$

and

$$y_{H_2} = \frac{P_T - P_{CH_3NH_2}}{P_T} = \frac{2.14 - 0.517}{2.14} = 0.758$$

Equation (3.15) was used to estimate the diffusivity of hydrogen deuteride in the mixture as follows

$$D_{mix} = \frac{1}{\frac{y_{H_2}}{D_{HD-H_2}} + \frac{y_{CH_3NH_2}}{D_{CH_3NH_2-HD}}}$$

$$= \frac{1}{\frac{0.758}{0.416} + \frac{0.242}{0.158}} \qquad (3.15)$$

$$= 0.298 \frac{cm^2}{s}$$

Viscosity of Gas Phase

1. Estimation of the Viscosity of Pure H_2 6

The following correlation (23) was used.

$$\mu_{H_2} = 8.411 \times 10^{-3}\left(\frac{T}{273.2}\right)^{0.695}$$

$$= 8.411 \times 10^{-3}\left(\frac{253.1}{273.2}\right)^{0.695} = 0.00789 \text{ cp} \tag{B.6}$$

2. Estimation of the Viscosity of Pure CH_3NH_2

The Bromley and Wilke modification of the Hirschfelder method (24) was used, as shown below.

$$\mu = \frac{0.0333(MT_C)^{1/2}}{V_C^{2/3}} (F(1.33\ T_r)) \tag{B.7}$$

where μ = viscosity (cp)

T_C = critical temperature (°K)

V_C = critical volume (cc/g-mole)

$F(1.33\ T_r) = 1.058\ T_r^{0.645} - \dfrac{0.261}{(1.9\ T_r)^{0.9 \log (1.9\ T_r)}}$

T_r = reduced temperature

The required constants for aminomethane are 7

T_C = 430.0 °K

V_C = 143.8 cc/g-mole

Calculation of the reduced temperature of CH_3NH_2 yielded

$$T_r = \frac{T}{T_C} = \frac{253.1}{430.0} = 0.589$$

Therefore

$$F(1.33\ T_r) = 1.058(0.589)^{0.645} - \frac{0.261}{(1.9 \times 0.589)^{0.9 \log (1.9 \times 0.589)}}$$

$$= 0.492$$

and

$$\mu_{CH_3NH_2} = \frac{0.00333(31.1 \times 430.0)^{1/2}}{(143.8)^{2/3}} (0.492)$$

$$= 0.00690 \text{ cp}$$

3. Estimation of the Viscosity of the Mixture

The viscosity of the mixture was estimated using the following equation (24).

$$\mu_{mix} = \frac{\mu_1}{1 + \frac{(y_2/y_1)[1 + (\mu_1/\mu_2)^{1/2}(M_2/M_1)^{1/4}]^2}{(4/\sqrt{2})[1 + (M_1/M_2)]^{1/2}}}$$

$$+ \frac{\mu_2}{1 + \frac{(y_1/y_2)[1 + (\mu_2/\mu_1)^{1/2}(M_1/M_2)^{1/4}]^2}{(\frac{4}{\sqrt{2}})[1 + (M_2/M_1)]^{1/2}}} \qquad \text{(B.8)}$$

$$= \frac{0.00798}{1 + \frac{(\frac{0.242}{0.758})[1 + (\frac{0.00798}{0.00690})^{1/2}(\frac{31.1}{2.0})^{1/4}]^2}{(\frac{4}{\sqrt{2}})[1 + (\frac{2.0}{31.1})]^{1/2}}}$$

$$+ \frac{0.00690}{1 + \frac{(\frac{0.758}{0.242})[1 + (\frac{0.00690}{0.00798})^{1/2}(\frac{2.0}{31.1})^{1/4}]^2}{(\frac{4}{\sqrt{2}})[1 + (\frac{31.1}{2.0})]^{1/2}}} = 0.00819 \text{ cp}$$

Gas Phase Reynold's Number

The gas phase Reynolds number may be expressed as

$$R_e = \frac{2R\, v_{av}\, \rho_G}{\mu_{mix}} \qquad (B.9)$$

where R_e = Reynold's number

R = radius of the sphere

v_{av} = average velocity of the gas in the absorption chamber (cm/sec)

ρ_G = density of the gas (g/cc)

1. Estimation of the Gas Velocity

The calibration curve for the gas rotameter reading of 16% of full scale indicated a flowrate of 5.2 ft^3/hr of air at 1 atm and 70°F. This was converted to the corresponding flowrate of the H_2-amine mixture at these standard conditions with the following equation.

$$\text{scc/s air} = \text{scc/s metered gas} \sqrt{\frac{SG}{1.0}\ \frac{T}{294.3}\ \frac{I}{P_T}} \qquad (B.10)$$

Therefore

Flowrate of H_2-amine mixture at standard [illegible]ions $= \dfrac{\dfrac{(5.2)(28317)\left(\frac{ft^3}{hr}\right)\left(\frac{cm^3}{ft^3}\right)}{3600\ \left(\frac{s}{hr}\right)}}{\sqrt{\left(\frac{9.03}{29}\right)\left(\frac{253}{294.3}\right)\left(\frac{1}{2.14}\right)}}$

$$= 116\ \frac{cm^3}{[illegible]}$$

The ideal gas law was then used to obtain the volumetric flowrate at the experimental conditions, yielding

$$\text{Volumetric Flowrate} = 116\ \frac{\frac{R_g T}{P}}{22.4}$$

$$= 50.1\ \frac{cm^3}{s}$$

The diameter of the absorption chamber was 7.62 cm, therefore

$$v_{av} = \frac{5.02}{\frac{\pi(7.62)^2}{4}} = 1.1\ \frac{cm}{s}$$

2. Estimation of the Gas Density

The molecular weight of the gas mixture was calculated as follows.

$$M_{mix} = M_{H_2}(y_{H_2}) + M_{CH_3NH_2}(y_{CH_3NH_2})$$

$$= 2.0(0.758) + 31.1(0.242) = 9.04\ \frac{g}{mol}$$

Using the ideal gas law the gas density was

$$\rho_G = \frac{n\ M_{mix}}{V} = \frac{P\ M_{mix}}{RT}\ atm\ \frac{g}{mol}\ \frac{mol\ °K}{cm^3\ atm}\ \frac{1}{°K}$$

$$= \frac{(2.14)(9.04)}{(82.06)(253.1)} = 9.3 \times 10^{-4}\ \frac{g}{cc}$$

Calculation of Reynolds number yielded

$$R_e = \frac{(2)(1.905)(1.1)(9.3 \times 10^{-4})}{(0.00819) \times 10^{-2}} \; \text{cm} \; \frac{\text{cm}}{\text{s}} \; \frac{\text{g}}{\text{cm}^3} \; \frac{\text{cm s}}{\text{g}}$$

$$= 47.6$$

Equation (3.16) was then evaluated to yield a value of the gas phase mass transfer coefficient as follows.

$$k_C = \frac{D_{mix}}{R} [1 + 0.276\, R_e^{1/2} (\frac{\mu_{mix}}{\rho_G\, D_{mix}})^{1/3}]$$

$$= \frac{0.298}{1.905} [1 + 0.276(47.6)^{1/2} (\frac{8.19 \times 10^{-5}}{9.3 \times 10^{-4}(0.298)})^{1/3}] \qquad (3.16)$$

$$= 0.355 \; \frac{\text{g-mole}}{\text{s cm}^2 \; \frac{\text{g-mole}}{\text{cm}^3}}$$

and

$$k_G = \frac{k_C}{R_g\, T}$$

$$k_G = \frac{0.355}{82.06(253.1)} \; \frac{\text{mol} \cdot \text{cm}^3}{\text{s cm}^2 \; \text{mol}} \; \frac{\text{mol °K}}{\text{cm}^3 \; \text{atm}} \; \frac{1}{\text{°K}}$$

$$= 1.70 \times 10^{-5} \; \frac{\text{mol}}{\text{s cm}^2 \; \text{atm}}$$

Substitution of k_G and K_L in Equation (3.13) yielded a value of k_L, as follows

$$\frac{1}{k_L} = \frac{1}{K_L} - \frac{\rho_L}{H\,k_g}$$

$$= \frac{1}{0.2298} - \frac{\frac{0.7110}{31.1}}{(7290)(1.70 \times 10^{-5})} \qquad (3.13)$$

$$= 4.168 \text{ s/cm}$$

or

$$k_L = 0.2399 \text{ cm/s}$$

B-4 Estimation of the First Order Rate Constant

Since the reaction occurred in the fast reaction regime; Equation (2.34) was used to evaluate the rate constant. The diffusivity of HD in aminomethane was estimated using the method described by Kalra (12), as follows.

$$\log_{10} D_{H_2} = -2.25564 - 0.432524 \left(\frac{1000}{T}\right)$$

$$= -2.25564 - 0.432524 \left(\frac{1000}{253.1}\right) \qquad (B.11)$$

$$= -3.9644$$

or

$$D_{H_2} = 1.085 \times 10^{-4} \text{ cm}^2\text{/s}$$

The diffusivity of HD in aminomethane was expressed as a fraction of that for H_2 as

$$D_{HD} = 0.9102\ D_{H_2}$$

$$= 0.9102\ (1.085 \times 10^{-4})$$

$$= 9.87 \times 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$$

Equation (2.34) was solved for k_1 to yield

$$k_L = \sqrt{k_1 D_{HD}} \tag{2.34}$$

therefore

$$k_1 = \frac{k_L^{\,2}}{D_{HD}}$$

$$= \frac{(0.2399)^2}{9.87 \times 10^{-5}}$$

$$k_1 = 583\ \mathrm{s}^{-1}$$

APPENDIX C

DETAILED EXPERIMENTAL DATA

```
                    RUN NO.  1  JUNE 05/74

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                            0.000
  POTASSIUM AMIDE                                          0.310
SYSTEM TEMPERATURE (DEG C)                                -41.9

TOTAL INITIAL PRESSURE (ATM)                               1.589
GAS VOLUME (CC)                                            2530.7
INTERFACIAL AREA (SQ.CM)                                   46.10
MONOMETHYLAMINE DENSITY (G/CC)                             0.7352

LIQUID FLOWRATE (CC/SEC)                                   0.258
GAS FLOWRATE (CC/SEC)                                      50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                9471.2
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                           0.680E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                  21.3
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)               130.6
MOLE FRACTION HYDROGEN IN GAS PHASE                        0.906
MOLE FRACTION AMINE IN GAS PHASE                           0.094

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                 0.4176
VISCOSITY OF HYDROGEN GAS (CP)                             0.00751
VISCOSITY OF AMINE VAPOR (CP)                              0.00630
VISCOSITY OF GAS MIXTURE (CP)                              0.00779

DENSITY OF GAS PHASE (G/CC)                                0.00039
GAS PHASE REYNOLD'S NUMBER                                 21.2
OVERALL LIQUID PHASE TRANSFER                              0.0937
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                        0.4373
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                 0.0947
FIRST ORDER RATE CONSTANT (1/SEC)                          131.7


     TIME        GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
     (SEC)       CONCENTRATION (PPM)
       0.0              477.1                0.0000
     400.0              456.7               -0.0458
     950.0              448.8               -0.0642
    1300.0              434.4               -0.0984
    2200.0              411.8               -0.1546
    3100.0              384.1               -0.2282
    3800.0              356.0               -0.3089
    4400.0              345.6               -0.3403
    5800.0              312.0               -0.4496
    6700.0              289.7               -0.5296
    7600.0              271.9               -0.5981
    8500.0              255.6               -0.6654
    9400.0              237.2               -0.7471
   10300.0              220.1               -0.8298
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```
   TIME         GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
   (SEC)        CONCENTRATION (PPM)
  11200.0              206.8                -0.8987
  11800.0              194.5                -0.9674
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                    RUN NO.   2  JUNE 18/74

 CATALYST CONCENTRATION (M EQ/G)
    LITHIUM AMIDE                                              0.000
    POTASSIUM AMIDE                                            0.310
 SYSTEM TEMPERATURE (DEG C)                                    -25.4

 TOTAL INITIAL PRESSURE (ATM)                                  1.956
 GAS VOLUME (CC)                                               2520.7
 INTERFACIAL AREA (SQ.CM)                                      46.06
 MONOMETHYLAMINE DENSITY (G/CC)                                0.7170

 LIQUID FLOWRATE (CC/SEC)                                      0.278
 GAS FLOWRATE (CC/SEC)                                         50.2
 HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                   7757.6
 HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                              0.907E-04

 GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                     25.2
 LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                  131.6
 MOLE FRACTION HYDROGEN IN GAS PHASE                           0.800
 MOLE FRACTION AMINE IN GAS PHASE                              0.200

 DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                    0.3304
 VISCOSITY OF HYDROGEN GAS (CP)                                0.00786
 VISCOSITY OF AMINE VAPOR (CP)                                 0.00675
 VISCOSITY OF GAS MIXTURE (CP)                                 0.00812

 DENSITY OF GAS PHASE (G/CC)                                   0.00075
 GAS PHASE REYNOLD'S NUMBER                                    38.7
 OVERALL LIQUID PHASE TRANSFER                                 0.1765
   COEFFICIENT (CM/SEC)

 GAS PHASE MASS TRANSFER COEFFICIENT                           0.3796
   (G MOLE/(SEC SQ.CM(G MOLE/CC)))
 LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                    0.1817
 FIRST ORDER RATE CONSTANT (1/SEC)                             363.6


    TIME          GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
    (SEC)         CONCENTRATION (PPM)
      0.0                361.9                  0.0000
    890.0                312.9                 -0.1571
   1790.0                268.4                 -0.3251
   2490.0                233.4                 -0.4804
   3490.0                198.7                 -0.6632
   4490.0                169.0                 -0.8510
   5190.0                148.2                 -1.0067
   6490.0                119.5                 -1.2729
   7490.0                103.0                 -1.4651
   8050.0                 97.6                 -1.5369
```

```
                    RUN NO.  3  JUNE 27/74

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                                0.000
  POTASSIUM AMIDE                                              0.310
SYSTEM TEMPERATURE (DEG C)                                    -38.1

TOTAL INITIAL PRESSURE (ATM)                                   1.697
GAS VOLUME (CC)                                                2528.4
INTERFACIAL AREA (SQ.CM)                                       46.06
MONOMETHYLAMINE DENSITY (G/CC)                                 0.7311

LIQUID FLOWRATE (CC/SEC)                                       0.230
GAS FLOWRATE (CC/SEC)                                          50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                    9041.8
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                               0.729E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                      22.5
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                   132.6
MOLE FRACTION HYDROGEN IN GAS PHASE                            0.889
MOLE FRACTION AMINE IN GAS PHASE                               0.111

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                     0.3902
VISCOSITY OF HYDROGEN GAS (CP)                                 0.00758
VISCOSITY OF AMINE VAPOR (CP)                                  0.00639
VISCOSITY OF GAS MIXTURE (CP)                                  0.00787

DENSITY OF GAS PHASE (G/CC)                                    0.00045
GAS PHASE REYNOLD'S NUMBER                                     24.4
OVERALL LIQUID PHASE TRANSFER                                  0.1141
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                            0.4182
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                     0.1157
FIRST ORDER RATE CONSTANT (1/SEC)                              183.3


   TIME          GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
   (SEC)         CONCENTRATION (PPM)
     0.0               260.3                 0.0000
   500.0               248.8                -0.0497
  2300.0               211.4                -0.2301
  3200.0               190.6                -0.3471
  4100.0               179.0                -0.4182
  5000.0               164.4                -0.5167
  5900.0               151.7                -0.6104
  6800.0               138.8                -0.7157
  7700.0               128.3                -0.8102
  8600.0               120.6                -0.8853
  9500.0               110.9                -0.9900
```

```
                         RUN NO. 4  JULY 11/74

 CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                               0.000
   POTASSIUM AMIDE                                             0.310
 SYSTEM TEMPERATURE (DEG C)                                   -21.2

 TOTAL INITIAL PRESSURE (ATM)                                  1.879
 GAS VOLUME (CC)                                               2517.8
 INTERFACIAL AREA (SQ.CM)                                      46.03
 MONOMETHYLAMINE DENSITY (G/CC)                                0.7123

 LIQUID FLOWRATE (CC/SEC)                                      0.206
 GAS FLOWRATE (CC/SEC)                                         50.2
 HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                   7388.2
 HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                              0.969E-04

 GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                     26.6
 LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                  133.6
 MOLE FRACTION HYDROGEN IN GAS PHASE                           0.741
 MOLE FRACTION AMINE IN GAS PHASE                              0.259

 DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                    0.3279
 VISCOSITY OF HYDROGEN GAS (CP)                                0.00795
 VISCOSITY OF AMINE VAPOR (CP)                                 0.00686
 VISCOSITY OF GAS MIXTURE (CP)                                 0.00812

 DENSITY OF GAS PHASE (G/CC)                                   0.00086
 GAS PHASE REYNOLD'S NUMBER                                    44.6
 OVERALL LIQUID PHASE TRANSFER                                 0.2043
   COEFFICIENT (CM/SEC)

 GAS PHASE MASS TRANSFER COEFFICIENT                           0.3821
   (G MOLE/(SEC SQ.CM(G MOLE/CC)))
 LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                    0.2115
 FIRST ORDER RATE CONSTANT (1/SEC)                             461.5


     TIME         GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
    (SEC)         CONCENTRATION (PPM)
      0.0               436.5                0.0000
    500.0               399.0               -0.0959
   1000.0               359.7               -0.2074
   1500.0               320.9               -0.3311
   2000.0               293.1               -0.4304
   2900.0               242.1               -0.6428
   3800.0               202.1               -0.8485
   4800.0               165.1               -1.0849
   5800.0               131.9               -1.3587
   6800.0               112.7               -1.5602
   7800.0                93.4               -1.8144
   8800.0                77.4               -2.0883
  10300.0                61.2               -2.4729
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                 RUN NO.  5  JULY 12/74

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                          0.000
  POTASSIUM AMIDE                                        0.310
SYSTEM TEMPERATURE (DEG C)                              -52.9

TOTAL INITIAL PRESSURE (ATM)                             1.671
GAS VOLUME (CC)                                          2510.2
INTERFACIAL AREA (SQ.CM)                                 46.10
MONOMETHYLAMINE DENSITY (G/CC)                           0.7468

LIQUID FLOWRATE (CC/SEC)                                 0.216
GAS FLOWRATE (CC/SEC)                                    50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              10853.0
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.549E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                19.6
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             134.6
MOLE FRACTION HYDROGEN IN GAS PHASE                      0.957
MOLE FRACTION AMINE IN GAS PHASE                         0.043

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.3945
VISCOSITY OF HYDROGEN GAS (CP)                           0.00724
VISCOSITY OF AMINE VAPOR (CP)                            0.00598
VISCOSITY OF GAS MIXTURE (CP)                            0.00743

DENSITY OF GAS PHASE (G/CC)                              0.00030
GAS PHASE REYNOLD'S NUMBER                               16.9
OVERALL LIQUID PHASE TRANSFER                            0.0592
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                      0.4093
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.0595
FIRST ORDER RATE CONSTANT (1/SEC)                        64.4


   TIME         GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
  (SEC)         CONCENTRATION (PPM)
    0.0               331.2                0.0000
  800.0               320.9               -0.0334
 1700.0               312.0               -0.0636
 2600.0               298.6               -0.1105
 3500.0               290.1               -0.1412
 4400.0               277.9               -0.1875
 6200.0               257.4               -0.2700
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                    RUN NO.  6  FEB. 05/75

    CATALYST CONCENTRATION (M EQ/G)
      LITHIUM AMIDE                                          0.300
      POTASSIUM AMIDE                                        0.300
    SYSTEM TEMPERATURE (DEG C)                               -24.8

    TOTAL INITIAL PRESSURE (ATM)                             2.057
    GAS VOLUME (CC)                                          2550.7
    INTERFACIAL AREA (SQ.CM)                                 46.07
    MONOMETHYLAMINE DENSITY (G/CC)                           0.7164

    LIQUID FLOWRATE (CC/SEC)                                 0.270
    GAS FLOWRATE (CC/SEC)                                    50.2
    HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              7706.7
    HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.915E-04

    GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                24.1
    LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             125.0
    MOLE FRACTION HYDROGEN IN GAS PHASE                      0.804
    MOLE FRACTION AMINE IN GAS PHASE                         0.196

    DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.3184
    VISCOSITY OF HYDROGEN GAS (CP)                           0.00787
    VISCOSITY OF AMINE VAPOR (CP)                            0.00676
    VISCOSITY OF GAS MIXTURE (CP)                            0.00814

    DENSITY OF GAS PHASE (G/CC)                              0.00077
    GAS PHASE REYNOLD'S NUMBER                               39.9
    OVERALL LIQUID PHASE TRANSFER                            0.1102
      COEFFICIENT (CM/SEC)

    GAS PHASE MASS TRANSFER COEFFICIENT                      0.3693
      (G MOLE/(SEC SQ.CM(G MOLE/CC)))
    LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.1122
    FIRST ORDER RATE CONSTANT (1/SEC)                        137.4


      TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
      (SEC)         CONCENTRATION (PPM)
        0.0               488.4                 0.0000
      300.0               477.0                -0.0250
      600.0               454.6                -0.0757
      950.0               437.5                -0.1161
     1200.0               430.2                -0.1339
     1790.0               409.7                -0.1857
     2200.0               386.4                -0.2682
     2700.0               362.4                -0.3167
     3600.0               321.1                -0.4467
     4500.0               283.2                -0.5833
     5400.0               275.2                -0.6146
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                    RUN NO.  7  FEB. 06/75

 CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                               0.300
   POTASSIUM AMIDE                                             0.300
 SYSTEM TEMPERATURE (DEG C)                                    -32.8

 TOTAL INITIAL PRESSURE (ATM)                                  1.761
 GAS VOLUME (CC)                                               2532.6
 INTERFACIAL AREA (SQ.CM)                                      46.10
 MONOMETHYLAMINE DENSITY (G/CC)                                0.7252

 LIQUID FLOWRATE (CC/SEC)                                      0.300
 GAS FLOWRATE (CC/SEC)                                         50.2
 HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                   8472.2
 HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                              0.801E-04

 GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                     22.4
 LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                  126.0
 MOLE FRACTION HYDROGEN IN GAS PHASE                           0.853
 [illegible]LE FRACTION AMINE IN GAS PHASE                     0.147

 [illegible]FUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)            0.3737
 VISCOSITY OF HYDROGEN GAS (CP)                                0.00770
 VISCOSITY OF AMINE VAPOR (CP)                                 0.00654
 VISCOSITY OF GAS MIXTURE (CP)                                 0.00799

 DENSITY OF GAS PHASE (G/CC)                                   0.00056
 GAS PHASE REYNOLD'S NUMBER                                    29.3
 OVERALL LIQUID PHASE TRANSFER                                 0.0864
   COEFFICIENT (CM/SEC)

 GAS PHASE MASS TRANSFER COEFFICIENT                           0.4099
   (G MOLE/(SEC SQ.CM(G MOLE/CC)))
 LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                    0.0874
 FIRST ORDER RATE CONSTANT (1/SEC)                             95.3


     TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
     (SEC)         CONCENTRATION (PPM)
       0.0               454.6                  0.0000
     500.0               439.3                 -0.0360
    1000.0               428.4                 -0.0625
    1500.0               413.4                 -0.1002
    2000.0               405.4                 -0.1208
    2900.0               356.4                 -0.2578
    3800.0               342.6                 -0.2999
    4700.0               317.3                 -0.3823
    5600.0               296.8                 -0.4544
    6500.0               271.2                 -0.5522
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                    RUN NO.  8  FEB. 14/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                          0.300
  POTASSIUM AMIDE                                        0.300
SYSTEM TEMPERATURE (DEG C)                               -38.7

TOTAL INITIAL PRESSURE (ATM)                             1.862
GAS VOLUME (CC)                                          2536.9
INTERFACIAL AREA (SQ.CM)                                 46.08
MONOMETHYLAMINE DENSITY (G/CC)                           0.7316

LIQUID FLOWRATE (CC/SEC)                                 0.238
GAS FLOWRATE (CC/SEC)                                    50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              9099.1
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.722E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                21.4
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             127.0
MOLE FRACTION HYDROGEN IN GAS PHASE                      0.902
MOLE FRACTION AMINE IN GAS PHASE                         0.098

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.3688
VISCOSITY OF HYDROGEN GAS (CP)                           0.00756
VISCOSITY OF AMINE VAPOR (CP)                            0.00637
VISCOSITY OF GAS MIXTURE (CP)                            0.00786

DENSITY OF GAS PHASE (G/CC)                              0.00046
GAS PHASE REYNOLD'S NUMBER                               24.9
OVERALL LIQUID PHASE TRANSFER                            0.0669
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                      0.3999
 (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.0674
FIRST ORDER RATE CONSTANT (1/SEC)                        62.8


   TIME        GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
   (SEC)       CONCENTRATION (PPM)
     0.0             485.0               0.0000
   500.0             475.8              -0.0202
  1300.0             445.2              -0.0899
  2100.0             433.0              -0.1192
  2900.0             413.3              -0.1680
  3700.0             395.6              -0.2144
  4500.0             377.1              -0.2650
  5300.0             357.0              -0.3231
  6100.0             342.1              -0.3687
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                        RUN NO.  9  MAR. 06/75

  CATALYST CONCENTRATION (M EQ/G)
    LITHIUM AMIDE                                                 0.300
    POTASSIUM AMIDE                                               0.300
  SYSTEM TEMPERATURE (DEG C)                                      -50.6

  TOTAL INITIAL PRESSURE (ATM)                                    1.699
  GAS VOLUME (CC)                                                 2530.7
  INTERFACIAL AREA (SQ.CM)                                        46.09
  MONOMETHYLAMINE DENSITY (G/CC)                                  0.7444

  LIQUID FLOWRATE (CC/SEC)                                        0.217
  GAS FLOWRATE (CC/SEC)                                           50.2
  HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                     10549.0
  HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                                0.575E-04

  GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                       19.1
  LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                    128.0
  MOLE FRACTION HYDROGEN IN GAS PHASE                             0.950
  MOLE FRACTION AMINE IN GAS PHASE                                0.050

  DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                      0.3907
  VISCOSITY OF HYDROGEN GAS (CP)                                  0.00730
  VISCOSITY OF AMINE VAPOR (CP)                                   0.00604
  VISCOSITY OF GAS MIXTURE (CP)                                   0.00751

  DENSITY OF GAS PHASE (G/CC)                                     0.00032
  GAS PHASE REYNOLD'S NUMBER                                      17.9
  OVERALL LIQUID PHASE TRANSFER                                   0.0395
    COEFFICIENT (CM/SEC)

  GAS PHASE MASS TRANSFER COEFFICIENT                             0.4079
    (G MOLE/(SEC SQ.CM(G MOLE/CC)))
  LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                      0.0397
  FIRST ORDER RATE CONSTANT (1/SEC)                               27.3


     TIME           GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
     (SEC)          CONCENTRATION (PPM)
       0.0                 460.1                  0.0000
     800.0                 444.4                 -0.0363
    1600.0                 437.8                 -0.0519
    2400.0                 422.7                 -0.0887
    3200.0                 418.1                 -0.1001
    4000.0                 409.6                 -0.1217
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                   RUN NO. 10  MAR. 06/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                                     0.300
  POTASSIUM AMIDE                                                   0.300
SYSTEM TEMPERATURE (DEG C)                                          -51.5

TOTAL INITIAL PRESSURE (ATM)                                        1.778
GAS VOLUME (CC)                                                     2530.7
INTERFACIAL AREA (SQ.CM)                                            45.96
MONOMETHYLAMINE DENSITY (G/CC)                                      0.7453

LIQUID FLOWRATE (CC/SEC)                                            0.075
GAS FLOWRATE (CC/SEC)                                               50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                         10672.0
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                                    0.564E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                           19.0
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                        129.0
MOLE FRACTION HYDROGEN IN GAS PHASE                                 0.956
MOLE FRACTION AMINE IN GAS PHASE                                    0.044

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                          0.3733
VISCOSITY OF HYDROGEN GAS (CP)                                      0.00727
VISCOSITY OF AMINE VAPOR (CP)                                       0.00601
VISCOSITY OF GAS MIXTURE (CP)                                       0.00747

DENSITY OF GAS PHASE (G/CC)                                         0.00032
GAS PHASE REYNOLD'S NUMBER                                          17.9
OVERALL LIQUID PHASE TRANSFER                                       0.0405
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                                 0.3928
 (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                          0.0407
FIRST ORDER RATE CONSTANT (1/SEC)                                   29.2


   TIME          GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
   (SEC)         CONCENTRATION (PPM)
     0.0               469.8                  0.0000
   500.0               465.6                 -0.0094
  1300.0               453.3                 -0.0373
  2100.0               443.6                 -0.0599
  3100.0               435.1                 -0.0800
  3700.0               419.4                 -0.1187
  4700.0               416.5                 -0.1258
  5300.0               401.5                 -0.1644
  6100.0               395.3                 -0.1807
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                          RUN NO. 11  MAR. 15/75

   CATALYST CONCENTRATION (M EQ/G)
     LITHIUM AMIDE                                                 0.300
     POTASSIUM AMIDE                                               0.300
   SYSTEM TEMPERATURE (DEG C)                                      -17.0

   TOTAL INITIAL PRESSURE (ATM)                                    2.008
   GAS VOLUME (CC)                                                 2519.5
   INTERFACIAL AREA (SQ.CM)                                        46.06
   MONOMETHYLAMINE DENSITY (G/CC)                                  0.7075

   LIQUID FLOWRATE (CC/SEC)                                        0.274
   GAS FLOWRATE (CC/SEC)                                           50.2
   HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                     7036.1
   HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                                0.103E-03

   GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                       26.8
   LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                    130.0
   MOLE FRACTION HYDROGEN IN GAS PHASE                             0.699
   MOLE FRACTION AMINE IN GAS PHASE                                0.301

   DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                      0.3041
   VISCOSITY OF HYDROGEN GAS (CP)                                  0.00804
   VISCOSITY OF AMINE VAPOR (CP)                                   0.00698
   VISCOSITY OF GAS MIXTURE (CP)                                   0.00815

   DENSITY OF GAS PHASE (G/CC)                                     0.00102
   GAS PHASE REYNOLD'S NUMBER                                      52.7
   OVERALL LIQUID PHASE TRANSFER                                   0.1450
     COEFFICIENT (CM/SEC)

   GAS PHASE MASS TRANSFER COEFFICIENT                             0.3650
     (G MOLE/(SEC SQ.CM(G MOLE/CC)))
   LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                      0.1490
   FIRST ORDER RATE CONSTANT (1/SEC)                               214.5


      TIME         GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
      (SEC)        CONCENTRATION (PPM)
        0.0              476.6                  0.0000
      600.0              427.2                 -0.1164
     1200.0              386.3                 -0.2242
     1800.0              348.8                 -0.3342
     2750.0              303.8                 -0.4847
     3000.0              291.8                 -0.5290
     3600.0              260.0                 -0.6568
     3750.0              251.8                 -0.6929
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                    RUN NO. 12  APR. 05/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                              0.430
  POTASSIUM AMIDE                                            0.430
SYSTEM TEMPERATURE (DEG C)                                   -39.1

TOTAL INITIAL PRESSURE (ATM)                                 1.863
GAS VOLUME (CC)                                              2532.4
INTERFACIAL AREA (SQ.CM)                                     46.09
MONOMETHYLAMINE DENSITY (G/CC)                               0.7321

LIQUID FLOWRATE (CC/SEC)                                     0.264
GAS FLOWRATE (CC/SEC)                                        50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  9150.7
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.716E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    21.8
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 130.0
MOLE FRACTION HYDROGEN IN GAS PHASE                          0.905
MOLE FRACTION AMINE IN GAS PHASE                             0.095

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.3614
VISCOSITY OF HYDROGEN GAS (CP)                               0.00755
VISCOSITY OF AMINE VAPOR (CP)                                0.00636
VISCOSITY OF GAS MIXTURE (CP)                                0.00785

DENSITY OF GAS PHASE (G/CC)                                  0.00046
GAS PHASE REYNOLD'S NUMBER                                   24.6
OVERALL LIQUID PHASE TRANSFER                                0.0670
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                          0.3927
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.0675
FIRST ORDER RATE CONSTANT (1/SEC)                            63.6


    TIME          GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
    (SEC)         CONCENTRATION (PPM)
      0.0               492.5                  0.0000
    800.0               476.2                 -0.0351
   1600.0               456.6                 -0.0793
   2400.0               438.3                 -0.1223
   3200.0               415.5                 -0.1787
   4000.0               396.9                 -0.2269
   4830.0               378.8                 -0.2763
   5600.0               361.6                 -0.3257
   6400.0               343.2                 -0.3814
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                    RUN NO. 13  APR. 11/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                          0.430
  POTASSIUM AMIDE                                        0.430
SYSTEM TEMPERATURE (DEG C)                              -17.8

TOTAL INITIAL PRESSURE (ATM)                             2.150
GAS VOLUME (CC)                                          2537.6
INTERFACIAL AREA (SQ.CM)                                 46.05
MONOMETHYLAMINE DENSITY (G/CC)                           0.7083

LIQUID FLOWRATE (CC/SEC)                                 0.282
GAS FLOWRATE (CC/SEC)                                    50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              7095.8
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.102E-03

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                26.9
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             131.0
MOLE FRACTION HYDROGEN IN GAS PHASE                      0.729
MOLE FRACTION AMINE IN GAS PHASE                         0.271

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.2921
VISCOSITY OF HYDROGEN GAS (CP)                           0.00803
VISCOSITY OF AMINE VAPOR (CP)                            0.00696
VISCOSITY OF GAS MIXTURE (CP)                            0.00819

DENSITY OF GAS PHASE (G/CC)                              0.00101
GAS PHASE REYNOLD'S NUMBER                               51.7
OVERALL LIQUID PHASE TRANSFER                            0.1441
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                      0.3526
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.1481
FIRST ORDER RATE CONSTANT (1/SEC)                        214.4


   TIME         GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
   (SEC)        CONCENTRATION (PPM)
     0.0              494.4               0.0000
   600.0              450.5              -0.0988
  1200.0              417.3              -0.1802
  1800.0              381.5              -0.2764
  2400.0              343.9              -0.3886
  3000.0              304.4              -0.5215
  3600.0              283.2              -0.6009
  4200.0              259.3              -0.6992
  4800.0              238.2              -0.7943
  5400.0              214.4              -0.9135
  6000.0              194.0              -1.0290
  6600.0              178.1              -1.1286
  7200.0              159.8              -1.2582
  7700.0              146.4              -1.3645
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                    RUN NO. 14  APR. 23/75

   CATALYST CONCENTRATION (M EQ/G)
     LITHIUM AMIDE                                          0.430
     POTASSIUM AMIDE                                        0.430
   SYSTEM TEMPERATURE (DEG C)                              -45.7

   TOTAL INITIAL PRESSURE (ATM)                             1.822
   GAS VOLUME (CC)                                          2525.6
   INTERFACIAL AREA (SQ.CM)                                 46.11
   MONOMETHYLAMINE DENSITY (G/CC)                           0.7392

   LIQUID FLOWRATE (CC/SEC)                                 0.251
   GAS FLOWRATE (CC/SEC)                                    50.2
   HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              9920.4
   HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.634E-04

   GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                20.7
   LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             132.0
   MOLE FRACTION HYDROGEN IN GAS PHASE                      0.936
   MOLE FRACTION AMINE IN GAS PHASE                         0.064

   DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.3695
   VISCOSITY OF HYDROGEN GAS (CP)                           0.00741
   VISCOSITY OF AMINE VAPOR (CP)                            0.00618
   VISCOSITY OF GAS MIXTURE (CP)                            0.00766

   DENSITY OF GAS PHASE (G/CC)                              0.00037
   GAS PHASE REYNOLD'S NUMBER                               20.6
   OVERALL LIQUID PHASE TRANSFER                            0.0498
     COEFFICIENT (CM/SEC)

   GAS PHASE MASS TRANSFER COEFFICIENT                      0.3940
     (G MOLE/(SEC SQ.CM(G MOLE/CC)))
   LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.0501
   FIRST ORDER RATE CONSTANT (1/SEC)                        39.5


       TIME          GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
       (SEC)         CONCENTRATION (PPM)
        0.0                504.7                 0.0000
      800.0                490.6                -0.0297
     1600.0                481.0                -0.0503
     2400.0                462.8                -0.0905
     3250.0                450.2                -0.1196
     4000.0                436.4                -0.1523
     4800.0                423.7                -0.1832
     5600.0                409.9                -0.2181
     6400.0                391.8                -0.2655
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                  RUN NO. 15   MAY 21/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                             0.630
  POTASSIUM AMIDE                                           0.630
SYSTEM TEMPERATURE (DEG C)                                  -44.6

TOTAL INITIAL PRESSURE (ATM)                                1.955
GAS VOLUME (CC)                                             2521.4
INTERFACIAL AREA (SQ.CM)                                    46.11
MONOMETHYLAMINE DENSITY (G/CC)                              0.7380

LIQUID FLOWRATE (CC/SEC)                                    0.253
GAS FLOWRATE (CC/SEC)                                       50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                 9783.5
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                            0.647E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                   21.0
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                132.0
MOLE FRACTION HYDROGEN IN GAS PHASE                         0.935
MOLE FRACTION AMINE IN GAS PHASE                            0.065

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                  0.3464
VISCOSITY OF HYDROGEN GAS (CP)                              0.00743
VISCOSITY OF AMINE VAPOR (CP)                               0.00621
VISCOSITY OF GAS MIXTURE (CP)                               0.00769

DENSITY OF GAS PHASE (G/CC)                                 0.00040
GAS PHASE REYNOLD'S NUMBER                                  22.0
OVERALL LIQUID PHASE TRANSFER                               0.0573
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                         0.3756
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                  0.0577
FIRST ORDER RA:E CONSTANT (1/SEC)                           51.3


     TIME           GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
     (SEC)          CONCENTRATION (PPM)
      0.0                 518.9                 0.0000
    800.0                 507.8                -0.0225
   1600.0                 490.2                -0.0594
   2450.0                 472.6                -0.0975
   3200.0                 456.2                -0.1346
   4000.0                 436.2                -0.1817
   4800.0                 421.0                -0.2189
   5600.0                 405.0                -0.2598
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                     RUN NO. 16    MAY 27/75
CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                              0.630
   POTASSIUM AMIDE                                            0.630
SYSTEM TEMPERATURE (DEG C)                                    -47.5

TOTAL INITIAL PRESSURE (ATM)                                  1.696
GAS VOLUME (CC)                                               2516.8
INTERFACIAL AREA (SQ.CM)                                      46.11
MONOMETHYLAMINE DENSITY (G/CC)                                0.7411

LIQUID FLOWRATE (CC/SEC)                                      0.247
GAS FLOWRATE (CC/SEC)                                         50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                   10149.0
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                              0.611E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                     20.5
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                  133.0
MOLE FRACTION HYDROGEN IN GAS PHASE                           0.939
MOLE FRACTION AMINE IN GAS PHASE                              0.061

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                    0.3927
VISCOSITY OF HYDROGEN GAS (CP)                                0.00736
VISCOSITY OF AMINE VAPOR (CP)                                 0.00612
VISCOSITY OF GAS MIXTURE (CP)                                 0.00760

DENSITY OF GAS PHASE (G/CC)                                   0.00034
GAS PHASE REYNOLDS'S NUMBER                                   19.0
OVERALL LIQUID PHASE TRANSFER                                 0.0531
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                           0.4117
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                    0.0534
FIRST ORDER RATE CONSTANT (1/SEC)                             46.5


      TIME            GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
     (SEC)            CONCENTRATION (PPM)
       0.0                  532.0                 0.0000
     800.0                  521.1                -0.0216
    1750.0                  499.8                -0.0651
    3200.0                  472.1                -0.1247
    4000.0                  455.3                -0.1626
    4800.0                  439.8                -0.1987
    5600.0                  426.6                -0.2309
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                     RUN NO. 17  JUNE 04/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                            0.630
  POTASSIUM AMIDE                                          0.630
SYSTEM TEMPERATURE (DEG C)                                 -23.1

TOTAL INITIAL PRESSURE (ATM)                               2.082
GAS VOLUME (CC)                                            2544.2
INTERFACIAL AREA (SQ.CM)                                   46.08
MONOMETHYLAMINE DENSITY (G/CC)                             0.7144

LIQUID FLOWRATE (CC/SEC)                                   0.296
GAS FLOWRATE (CC/SEC)                                      50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                7548.9
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                           0.941E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                  26.2
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)               134.0
MOLE FRACTION HYDROGEN IN GAS PHASE                        0.787
MOLE FRACTION AMINE IN GAS PHASE                           0.213

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                 0.3107
VISCOSITY OF HYDROGEN GAS (CP)                             0.00791
VISCOSITY OF AMINE VAPOR (CP)                              0.00681
VISCOSITY OF GAS MIXTURE (CP)                              0.00816

DENSITY OF GAS PHASE (G/CC)                                0.00083
GAS PHASE REYNOLD'S NUMBER                                 42.6
OVERALL LIQUID PHASE TRANSFER                              0.1319
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                        0.3642
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                 0.1350
FIRST ORDER RATE CONSTANT (1/SEC)                          193.4


   TIME          GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
  (SEC)          CONCENTRATION (PPM)
     0.0               510.1                0.0000
   600.0               468.3               -0.0904
  1200.0               432.1               -0.1758
  1800.0               394.6               -0.2729
  2400.0               370.8               -0.3396
  3000.0               343.6               -0.4218
  3600.0               311.7               -0.5278
  4400.0               277.5               -0.6554
  5200.0               258.8               -0.7325
  6000.0               228.8               -0.8708
  6800.0               194.5               -1.0564
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                      RUN NO. 18  JULY 01/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                                   0.630
  POTASSIUM AMIDE                                                 0.630
SYSTEM TEMPERATURE (DEG C)                                        -13.2

TOTAL INITIAL PRESSURE (ATM)                                      2.166
GAS VOLUME (CC)                                                   2524.3
INTERFACIAL AREA (SQ.CM)                                          46.08
MONOMETHYLAMINE DENSITY (G/CC)                                    0.7031

LIQUID FLOWRATE (CC/SEC)                                          0.313
GAS FLOWRATE (CC/SEC)                                             50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                       6736.1
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                                  0.109E-03

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                         28.9
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                      136.0
MOLE FRACTION HYDROGEN IN GAS PHASE                               0.664
MOLE FRACTION AMINE IN GAS PHASE                                  0.336

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                        0.2785
VISCOSITY OF HYDROGEN GAS (CP)                                    0.00812
VISCOSITY OF AMINE VAPOR (CP)                                     0.00709
VISCOSITY OF GAS MIXTURE (CP)                                     0.00818

DENSITY OF GAS PHASE (G/CC)                                       0.00119
GAS PHASE REYNOLD'S NUMBER                                        61.0
OVERALL LIQUID PHASE TRANSFER                                     0.1766
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                               0.3446
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                        0.1834
FIRST ORDER RATE CONSTANT (1/SEC)                                 306.9


   TIME          GAS PHASE DEUTERIUM        LN((Y-YE)/(YI-YE))
   (SEC)         CONCENTRATION (PPM)
     0.0                493.4                    0.0000
   700.0                442.9                   -0.1151
  1400.0                379.6                   -0.2809
  2100.0                326.6                   -0.4447
  2800.0                282.9                   -0.6035
  3500.0                250.4                   -0.7405
  4200.0                210.3                   -0.9401
  4900.0                177.3                   -1.1408
  5600.0                159.4                   -1.2693
  6300.0                142.4                   -1.4090
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                    RUN NO. 19  JULY 09/75

CATALYST CONCENTRATION (M.EQ/G)
  LITHIUM AMIDE                                          0.630
  POTASSIUM AMIDE                                        0.630
SYSTEM TEMPERATURE (DEG C)                              -40.0

TOTAL INITIAL PRESSURE (ATM)                             1.913
GAS VOLUME (CC)                                          2528.6
INTERFACIAL AREA (SQ.CM)                                 46.10
MONOMETHYLAMINE DENSITY (G/CC)                           0.7331

LIQUID FLOWRATE (CC/SEC)                                 0.263
GAS FLOWRATE (CC/SEC)                                    50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              9250.5
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.705E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                22.8
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             137.0
MOLE FRACTION HYDROGEN IN GAS PHASE                      0.912
MOLE FRACTION AMINE IN GAS PHASE                         0.088

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.3542
VISCOSITY OF HYDROGEN GAS (CP)                           0.00754
VISCOSITY OF AMINE VAPOR (CP)                            0.00634
VISCOSITY OF GAS MIXTURE (CP)                            0.00783

DENSITY OF GAS PHASE (G/CC)                              0.00045
GAS PHASE REYNOLD'S NUMBER                               24.3
OVERALL LIQUID PHASE TRANSFER                            0.0709
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                      0.3859
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.0715
FIRST ORDER RATE CONSTANT (1/SEC)                        72.5


   TIME        GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
   (SEC)       CONCENTRATION (PPM)
     0.0             524.4                  0.0000
  1400.0             481.7                 -0.0888
  2100.0             464.7                 -0.1267
  2900.0             445.3                 -0.1714
  3700.0             421.5                 -0.2296
  4600.0             398.9                 -0.2877
  5500.0             377.2                 -0.3473
  6000.0             367.1                 -0.3762
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                    RUN NO. 20  JULY 30/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                          1.660
  POTASSIUM AMIDE                                        0.390
SYSTEM TEMPERATURE (DEG C)                               -43.2

TOTAL INITIAL PRESSURE (ATM)                             1.901
GAS VOLUME (CC)                                          2519.2
INTERFACIAL AREA (SQ.CM)                                 46.12
MONOMETHYLAMINE DENSITY (G/CC)                           0.7365

LIQUID FLOWRATE (CC/SEC)                                 0.256
GAS FLOWRATE (CC/SEC)                                    50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              9620.6
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.664E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                20.9
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             130.0
MOLE FRACTION HYDROGEN IN GAS PHASE                      0.928
MOLE FRACTION AMINE IN GAS PHASE                         0.072

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.3566
VISCOSITY OF HYDROGEN GAS (CP)                           0.00746
VISCOSITY OF AMINE VAPOR (CP)                            0.00625
VISCOSITY OF GAS MIXTURE (CP)                            0.00773

DENSITY OF GAS PHASE (G/CC)                              0.00041
GAS PHASE REYNOLD'S NUMBER                               22.3
OVERALL LIQUID PHASE TRANSFER                            0.0140
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                      0.3851
  (G MOLE/(SEC.SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.0140
FIRST ORDER RATE CONSTANT (1/SEC)                        2.10


   TIME          GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-Y[illegible]
  (SEC)          CONCENTRATION (PPM)
     0.0               518.5                 0.0000
   600.0               517.1                -0.0028
  1300.0               513.0                -0.0111
  2000.0               508.8                -0.0196
  2800.0               499.0                -0.0399
  3700.0               493.8                -0.0508
  4600.0               488.4                -0.0624
  5550.0               484.6                -0.0706
  6400.0               484.3                -0.0713
  7300.0               480.7                -0.0789
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                    RUN NO. 21  AUG. 15/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                            1.660
  POTASSIUM AMIDE                                          0.390
SYSTEM TEMPERATURE (DEG C)                                -19.2

TOTAL INITIAL PRESSURE (ATM)                               2.137
GAS VOLUME (CC)                                            2517.5
INTERFACIAL AREA (SQ.CM)                                   46.07
MONOMETHYLAMINE DENSITY (G/CC)                             0.7100

LIQUID FLOWRATE (CC/SEC)                                   0.028
GAS FLOWRATE (CC/SEC)                                      50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                7214.9
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                           0.100E-03

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                  26.4
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)               130.2
MOLE FRACTION HYDROGEN IN GAS PHASE                        0.747
MOLE FRACTION AMINE IN GAS PHASE                           0.253

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                 0.2965
VISCOSITY OF HYDROGEN GAS (CP)                             0.00800
VISCOSITY OF AMINE VAPOR (CP)                              0.00692
VISCOSITY OF GAS MIXTURE (CP)                              0.00819

DENSITY OF GAS PHASE (G/CC)                                0.00095
GAS PHASE REYNOLD'S NUMBER                                 48.9
OVERALL LIQUID PHASE TRANSFER                              0.0343
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                        0.3551
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                 0.0346
FIRST ORDER RATE CONSTANT (1/SEC)                          11.5


   TIME          GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
   (SEC)         CONCENTRATION (PPM)
     0.0               505.8                  0.0000
  1300.0               493.8                 -0.0253
  3160.0               455.7                 -0.1103
  4800.0               421.1                 -0.1944
  6600.0               395.9                 -0.2604
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                         RUN NO. 22  AUG. 29/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                                1.660
  POTASSIUM AMIDE                                              0.390
SYSTEM TEMPERATURE (DEG C)                                     -26.4

TOTAL INITIAL PRESSURE (ATM)                                   1.955
GAS VOLUME (CC)                                                2526.2
INTERFACIAL AREA (SQ.CM)                                       46.09
MONOMETHYLAMINE DENSITY (G/CC)                                 0.7181

LIQUID FLOWRATE (CC/SEC)                                       0.304
GAS FLOWRATE (CC/SEC)                                          50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                    7847.7
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                               0.893E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                      24.8
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                   130.5
MOLE FRACTION HYDROGEN IN GAS PHASE                            0.810
MOLE FRACTION AMINE IN GAS PHASE                               0.190

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                     0.3327
VISCOSITY OF HYDROGEN GAS (CP)                                 0.00784
VISCOSITY OF AMINE VAPOR (CP)                                  0.00672
VISCOSITY OF GAS MIXTURE (CP)                                  0.00811

DENSITY OF GAS PHASE (G/CC)                                    0.00072
GAS PHASE REYNOLD'S NUMBER                                     37.4
OVERALL LIQUID PHASE TRANSFER                                  0.0267
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                            0.3806
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                     0.0268
FIRST ORDER RATE CONSTANT (1/SEC)                              7.50


   TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
   (SEC)         CONCENTRATION (PPM)
     0.0               491.7                 0.0000
  1000.0               487.5                -0.0091
  2000.0               471.2                -0.0451
  3000.0               458.5                -0.0738
  4000.0               445.5                -0.1042
  5000.0               430.4                -0.1407
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                         RUN NO. 23 SEPT. 26/75

 CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                              0.000
   POTASSIUM AMIDE                                            0.400
 SYSTEM TEMPERATURE (DEG C)                                   -48.4

 TOTAL INITIAL PRESSURE (ATM)                                 1.787
 GAS VOLUME (CC)                                              2511.6
 INTERFACIAL AREA (SQ.CM)                                     46.11
 MONOMETHYLAMINE DENSITY (G/CC)                               0.7420

 LIQUID FLOWRATE (CC/SEC)                                     0.245
 GAS FLOWRATE (CC/SEC)                                        50.2
 HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  10261.0
 HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.601E-04

 GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    17.7
 LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 116.2
 MOLE FRACTION HYDROGEN IN GAS PHASE                          0.945
 MOLE FRACTION AMINE IN GAS PHASE                             0.055

 DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.3741
 VISCOSITY OF HYDROGEN GAS (CP)                               0.00734
 VISCOSITY OF AMINE VAPOR (CP)                                0.00610
 VISCOSITY OF GAS MIXTURE (CP)                                0.00757

 DENSITY OF GAS PHASE (G/CC)                                  0.00034
 GAS PHASE REYNOLD'S NUMBER                                   19.2
 OVERALL LIQUID PHASE TRANSFER                                0.0772
   COEFFICIENT (CM/SEC)

 GAS PHASE MASS TRANSFER COEFFICIENT                          0.3958
   (G MOLE/(SEC SQ.CM(G MOLE/CC)))
 LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.0779
 FIRST ORDER RATE CONSTANT (1/SEC)                            100.8


     TIME          GAS PHASE DEUTERIUM     LN((Y-YE)/(YI-YE))
     (SEC)         CONCENTRATION (PPM)
       0.0               542.8                  0.0000
     630.0               532.5                 -0.0197
    1300.0               508.2                 -0.0681
    2100.0               484.4                 -0.1178
    3000.0               463.3                 -0.1640
    4000.0               435.9                 -0.2275
    5000.0               409.5                 -0.2929
    6000.0               387.2                 -0.3513
    7000.0               361.9                 -0.4222
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                    RUN NO. 24  OCT. 01/75

 CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                              0.000
   POTASSIUM AMIDE                                            0.400
 SYSTEM TEMPERATURE (DEG C)                                  -20.1

 TOTAL INITIAL PRESSURE (ATM)                                 2.141
 GAS VOLUME (CC)                                              2525.2
 INTERFACIAL AREA (SQ.CM)                                     46.05
 MONOMETHYLAMINE DENSITY (G/CC)                               0.7110

 LIQUID FLOWRATE (CC/SEC)                                     0.250
 GAS FLOWRATE (CC/SEC)                                        50.2
 HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  7290.3
 HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.987E-04

 GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    23.6
 LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 117.2
 MOLE FRACTION HYDROGEN IN GAS PHASE                          0.758
 MOLE FRACTION AMINE IN GAS PHASE                             0.242

 DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.2985
 VISCOSITY OF HYDROGEN GAS (CP)                               0.00798
 VISCOSITY OF AMINE VAPOR (CP)                                0.00690
 VISCOSITY OF GAS MIXTURE (CP)                                0.00819

 DENSITY OF GAS PHASE (G/CC)                                  0.00093
 GAS PHASE REYNOLD'S NUMBER                                   47.5
 OVERALL LIQUID PHASE TRANSFER                                0.2297
   COEFFICIENT (CM/SEC)

 GAS PHASE MASS TRANSFER COEFFICIENT                          0.3560
   (G MOLE/(SEC SQ.CM(G MOLE/CC)))
 LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.2397
 FIRST ORDER RATE CONSTANT (1/SEC)                            582.3


      TIME          GAS PHASE DEUTERIUM      LN((Y-YE)/(YI-YE))
     (SEC)          CONCENTRATION (PPM)
       0.0               463.1                  0.0000
     600.0               401.8                 -0.1504
    1300.0               328.3                 -0.3664
    2020.0               279.6                 -0.5406
    2700.0               239.2                 -0.7122
    3500.0               195.2                 -0.9407
    4300.0               161.6                 -1.1585
    5200.0               126.8                 -1.4489
    5900.0               113.2                 -1.5908
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                    RUN NO. 25  OCT. 04/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                             0.000
  POTASSIUM AMIDE                                           0.400
SYSTEM TEMPERATURE (DEG C)                                  -40.0

TOTAL INITIAL PRESSURE (ATM)                                1.941
GAS VOLUME (CC)                                             2517.6
INTERFACIAL AREA (SQ.CM)                                    46.08
MONOMETHYLAMINE DENSITY (G/CC)                              0.7331

LIQUID FLOWRATE (CC/SEC)                                    0.240
GAS FLOWRATE (CC/SEC)                                       50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                 9250.5
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                            0.705E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                   19.6
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                118.2
MOLE FRACTION HYDROGEN IN GAS PHASE                         0.913
MOLE FRACTION AMINE IN GAS PHASE                            0.087

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                  0.3492
VISCOSITY OF HYDROGEN GAS (CP)                              0.00753
VISCOSITY OF AMINE VAPOR (CP)                               0.00634
VISCOSITY OF GAS MIXTURE (CP)                               0.00782

DENSITY OF GAS PHASE (G/CC)                                 0.00045
GAS PHASE REYNOLD'S NUMBER                                  24.5
OVERALL LIQUID PHASE TRANSFER                               0.1061
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                         0.3817
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                  0.1076
FIRST ORDER RATE CONSTANT (1/SEC)                           164.1


    TIME          GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
   (SEC)          CONCENTRATION (PPM)
     0.0                485.8                 0.0000
   600.0                464.7                -0.0463
  2100.0                396.9                -0.2117
  3000.0                366.6                -0.2954
  3900.0                339.4                -0.3768
  4900.0                312.7                -0.4642
  5900.0                288.0                -0.5522
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                     RUN NO. 26  OCT. 09/75

CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                            0.000
   POTASSIUM AMIDE                                          0.400
 SYSTEM TEMPERATURE (DEG C)                                -29.6

TOTAL INITIAL PRESSURE (ATM)                                2.037
GAS VOLUME (CC)                                             2519.2
INTERFACIAL AREA (SQ.CM)                                    46.08
MONOMETHYLAMINE DENSITY (G/CC)                              0.7917

LIQUID FLOWRATE (CC/SEC)                                    0.261
GAS FLOWRATE (CC/SEC)                                       50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                 8155.7
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                            0.846E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                   22.0
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                119.2
MOLE FRACTION HYDROGEN IN GAS PHASE                         0.847
MOLE FRACTION AMINE IN GAS PHASE                            0.153

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                  0.3267
VISCOSITY OF HYDROGEN GAS (CP)                              0.00777
VISCOSITY OF AMINE VAPOR (CP)                               0.00663
VISCOSITY OF GAS MIXTURE (CP)                               0.00807

DENSITY OF GAS PHASE (G/CC)                                 0.00065
GAS PHASE REYNOLD'S NUMBER                                  34.0
OVERALL LIQUID PHASE TRANSFER                               0.1563
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                         0.3718
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                  0.1602
FIRST ORDER RATE CONSTANT (1/SEC)                           303.1


    TIME        GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
    (SEC)       CONCENTRATION (PPM)
      0.0             471.7                0.0000
    600.0             431.0               -0.0947
   1300.0             393.8               -0.1902
   5800.0             199.4               -0.9302
   6600.0             175.6               -1.0743
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                         RUN NO. 27  OCT. 10/75

    CATALYST CONCENTRATION (M EQ/G)
      LITHIUM AMIDE                                              0.860
      POTASSIUM AMIDE                                            0.500
    SYSTEM TEMPERATURE (DEG C)                                  -47.7

    TOTAL INITIAL PRESSURE (ATM)                                 1.875
    GAS VOLUME (CC)                                              2523.9
    INTERFACIAL AREA (SQ.CM)                                     46.09
    MONOMETHYLAMINE DENSITY (G/CC)                               0.7413

    LIQUID FLOWRATE (CC/SEC)                                     0.224
    GAS FLOWRATE (CC/SEC)                                        50.2
    HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  10171.0
    HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.609E-04

    GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    19.1
    LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 124.0
    MOLE FRACTION HYDROGEN IN GAS PHASE                          0.945
    MOLE FRACTION AMINE IN GAS PHASE                             0.055

    DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.3588
    VISCOSITY OF HYDROGEN GAS (CP)                               0.00736
    VISCOSITY OF AMINE VAPOR (CP)                                0.00612
    VISCOSITY OF GAS MIXTURE (CP)                                0.00759

    DENSITY OF GAS PHASE (G/CC)                                  0.00036
    GAS PHASE REYNOLD'S NUMBER                                   20.1
    OVERALL LIQUID PHASE TRANSFER                                0.0325
      COEFFICIENT (CM/SEC)

    GAS PHASE MASS TRANSFER COEFFICIENT                          0.3836
      (G MOLE/(SEC SQ.CM(G MOLE/CC)))
    LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.0327
    FIRST ORDER RATE CONSTANT (1/SEC)                            17.5


        TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
        (SEC)         CONCENTRATION (PPM)
         0.0                 508.1                 0.0000
      1000.0                 504.5                -0.0074
      2000.0                 494.7                -0.0277
      3000.0                 478.8                -0.0619
      4000.0                 468.7                -0.0841
      5000.0                 455.5                -0.1138
      6000.0                 443.8                -0.1410
      7000.0                 430.0                -0.1740
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                         RUN NO. 28 . NOV. 05/75

   CATALYST CONCENTRATION (M EQ/G)
     LITHIUM AMIDE                                                     0.860
     POTASSIUM AMIDE                                                   0.500
   SYSTEM TEMPERATURE (DEG C)                                          -20.6

   TOTAL INITIAL PRESSURE (ATM)                                        1.938
   GAS VOLUME (CC)                                                     2518.4
   INTERFACIAL AREA (SQ.CM)                                            46.06
   MONOMETHYLAMINE DENSITY (G/CC)                                      0.7115

   LIQUID FLOWRATE (CC/SEC)                                            0.277
   GAS FLOWRATE (CC/SEC)                                               50.2
   HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                         7331.8
   HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                                    0.979E-04

   GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                           25.0
   LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                        125.0
   MOLE FRACTION HYDROGEN IN GAS PHASE                                 0.740
   MOLE FRACTION AMINE IN GAS PHASE                                    0.260

   DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                          0.3223
   VISCOSITY OF HYDROGEN GAS (CP)                                      0.00796
   VISCOSITY OF AMINE VAPOR (CP)                                       0.00688
   VISCOSITY OF GAS MIXTURE (CP)                                       0.00814

   DENSITY OF GAS PHASE (G/CC)                                         0.00089
   GAS PHASE REYNOLD'S NUMBER                                          45.9
   OVERALL LIQUID PHASE TRANSFER                                       0.0913
     COEFFICIENT (CM/SEC)

   GAS PHASE MASS TRANSFER COEFFICIENT                                 [illegible]3778
     (G MOLE/(SEC SQ.CM(G MOLE/CC)))
   LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                          [illegible]0928
   FIRST ORDER RATE CONSTANT (1/SEC)                                   87.8


      TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
     (SEC)          CONCENTRATION (PPM)
       0.0                474.2                  0.0000
     800.0                438.3                 -0.0834
    2400.0                363.6                 -0.2827
    3200.0                342.8                 -0.3463
    4000.0                319.4                 -0.4225
    4800.0                290.9                 -0.5245
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                 RUN NO. 29  NOV. 17/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                               0.860
  POTASSIUM AMIDE                                             0.500
SYSTEM TEMPERATURE (DEG C)                                    -31.1

TOTAL INITIAL PRESSURE (ATM)                                  1.428
GAS VOLUME (CC)                                               2517.6
INTERFACIAL AREA (SQ.CM)                                      46.07
MONOMETHYLAMINE DENSITY (G/CC)                                0.7233

LIQUID FLOWRATE (CC/SEC)                                      0.258
GAS FLOWRATE (CC/SEC)                                         50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                   8301.5
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                              0.825E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                     22.9
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                  126.0
MOLE FRACTION HYDROGEN IN GAS PHASE                           0.800
MOLE FRACTION AMINE IN GAS PHASE                              0.200

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                    0.4347
VISCOSITY OF HYDROGEN GAS (CP)                                0.00773
VISCOSITY OF AMINE VAPOR (CP)                                 0.00659
VISCOSITY OF GAS MIXTURE (CP)                                 0.00795

DENSITY OF GAS PHASE (G/CC)                                   0.00056
GAS PHASE REYNOLD'S NUMBER                                    29.5
OVERALL LIQUID PHASE TRANSFER                                 0.0666
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                           0.4649
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                    0.0671
FIRST ORDER RATE CONSTANT (1/SEC)                             54.5


   TIME         GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
  (SEC)         CONCENTRATION (PPM)
     0.0               495.8               0.0000
   600.0               478.7              -0.0368
  1200.0               451.9              -0.0974
  2400.0               422.6              -0.1681
  3000.0               408.3              -0.2046
  3600.0               393.2              -0.2446
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                    RUN NO. 30  NOV. 21/75

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                              0.860
  POTASSIUM AMIDE                                            0.500
SYSTEM TEMPERATURE (DEG C)                                   -38.1

TOTAL INITIAL PRESSURE (ATM)                                 1.851
GAS VOLUME (CC)                                              2521.4
INTERFACIAL AREA (SQ.CM)                                     46.08
MONOMETHYLAMINE DENSITY (G/CC)                               0.7311

LIQUID FLOWRATE (CC/SEC)                                     0.243
GAS FLOWRATE (CC/SEC)                                        50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  9041.9
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.729E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    21.9
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 127.0
MOLE FRACTION HYDROGEN IN GAS PHASE                          0.898
MOLE FRACTION AMINE IN GAS PHASE                             0.102

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.3628
VISCOSITY OF HYDROGEN GAS (CP)                               0.00758
VISCOSITY OF AMINE VAPOR (CP)                                0.00639
VISCOSITY OF GAS MIXTURE (CP)                                0.00788

DENSITY OF GAS PHASE (G/CC)                                  0.00047
GAS PHASE REYNOLD'S NUMBER                                   25.3
OVERALL LIQUID PHASE TRANSFER                                0.0546
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                          0.3950
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.0550
FIRST ORDER RATE CONSTANT (1/SEC)                            41.3


    TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
   (SEC)          CONCENTRATION (PPM)
     0.0                 501.8                0.0000
   700.0                 488.6               -0.0280
  1400.0                 462.6               -0.0853
  2100.0                 457.8               -0.0963
  2800.0                 434.6               -0.1509
  3500.0                 424.2               -0.1764
  4200.0                 405.6               -0.2237
  4900.0                 397.6               -0.2449
  5600.0                 386.9               -0.2736
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                    RUN NO. 31 - NOV. 27/75
CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                            0.860
  POTASSIUM AMIDE                                          0.500
SYSTEM TEMPERATURE (DEG C)                                -10.2

TOTAL INITIAL PRESSURE (ATM)                               2.150
GAS VOLUME (CC)                                            2521.8
INTERFACIAL AREA (SQ.CM)                                   46.06
MONOMETHYLAMINE DENSITY (G/CC)                             0.6995

LIQUID FLOWRATE (CC/SEC)                                   0.295
GAS FLOWRATE (CC/SEC)                                      50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                6506.7
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                           0.114E-03

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                  27.9
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)               128.0
MOLE FRACTION HYDROGEN IN GAS PHASE                        0.608
MOLE FRACTION AMINE IN GAS PHASE                           0.392

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                 0.2697
VISCOSITY OF HYDROGEN GAS (CP)                             0.00819
VISCOSITY OF AMINE VAPOR (CP)                              0.00718
VISCOSITY OF GAS MIXTURE (CP)                              0.00815

DENSITY OF GAS PHASE (G/CC)                                0.00133
GAS PHASE REYNOLD'S NUMBER                                 68.4
OVERALL LIQUID PHASE TRANSFER                              0.1319
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                        0.3395
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                 0.1358
FIRST ORDER RATE CONSTANT (1/SEC)                          161.1


   TIME         GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
   (SEC)        CONCENTRATION (PPM)
     0.0              431.5                  0.0000
   500.0              404.8                 -0.0684
  1500.0              340.2                 -0.2565
  2000.0              310.7                 -0.3555
  2500.0              287.8                 -0.4401
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                    RUN NO. 32  FEB. 11/76
 CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                                  0.350
   POTASSIUM AMIDE                                                0.480
 SYSTEM TEMPERATURE (DEG C)                                       -45.0

 TOTAL INITIAL PRESSURE (ATM)                                     1.876
 GAS VOLUME (CC)                                                  2524.1
 INTERFACIAL AREA (SQ.CM)                                         46.08
 MONOMETHYLAMINE DENSITY (G/CC)                                   0.7385

 LIQUID FLOWRATE (CC/SEC)                                         0.225
 GAS FLOWRATE (CC/SEC)                                            50.2
 HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                      9844.5
 HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                                 0.641E-04

 GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                        20.3
 LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                     128.3
 MOLE FRACTION HYDROGEN IN GAS PHASE                              0.935
 MOLE FRACTION AMINE IN GAS PHASE                                 0.065

 DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                       0.3597
 VISCOSITY OF HYDROGEN GAS (CP)                                   0.00742
 VISCOSITY OF AMINE VAPOR (CP)                                    0.00620
 VISCOSITY OF GAS MIXTURE (CP)                                    0.00767

 DENSITY OF GAS PHASE (G/CC)                                      0.00038
 GAS PHASE REYNOLD'S NUMBER                                       21.2
 OVERALL LIQUID PHASE TRANSFER                                    0.0588
   COEFFICIENT (CM/SEC)

 GAS PHASE MASS TRANSFER COEFFICIENT                              0.3863
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
 LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                       0.0592
 FIRST ORDER RATE CONSTANT (1/SEC)                                54.5


     TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
     (SEC)         CONCENTRATION (PPM)
       0.0               493.0                 0.0000
     600.0               482.1                -0.0234
    1600.0               457.5                -0.0782
    2600.0               434.8                -0.1316
    3600.0               416.0                -0.1778
    4600.0               402.1                -0.2135
    5600.0               382.2                -0.2672
    6600.0               363.0                -0.3217
    7500.0               348.6                -0.3645
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                    RUN NO. 33  FEB. 19/76

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                          0.350
  POTASSIUM AMIDE                                        0.480
SYSTEM TEMPERATURE (DEG C)                               -23.7

TOTAL INITIAL PRESSURE (ATM)                             2.063
GAS VOLUME (CC)                                          2526.8
INTERFACIAL AREA (SQ.CM)                                 46.08
MONOMETHYLAMINE DENSITY (G/CC)                           0.7150

LIQUID FLOWRATE (CC/SEC)                                 0.272
GAS FLOWRATE (CC/SEC)                                    50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              7602.0
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.932E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                25.1
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             129.3
MOLE FRACTION HYDROGEN IN GAS PHASE                      0.792
MOLE FRACTION AMINE IN GAS PHASE                         0.208

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.3119
VISCOSITY OF HYDROGEN GAS (CP)                           0.00790
VISCOSITY OF AMINE VAPOR (CP)                            0.00680
VISCOSITY OF GAS MIXTURE (CP)                            0.00815

DENSITY OF GAS PHASE (G/CC)                              0.00081
GAS PHASE REYNOLD'S NUMBER                               41.6
OVERALL LIQUID PHASE TRANSFER                            0.1360
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                      0.3645
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.1393
FIRST ORDER RATE CONSTANT (1/SEC)                        207.8


     TIME         GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
    (SEC)         CONCENTRATION (PPM)
      0.0               458.0                0.0000
    600.0               421.9               -0.0869
   1200.0               384.9               -0.1847
   1800.0               356.7               -0.2664
   2400.0               321.8               -0.3776
   3100.0               291.4               -0.4857
   3800.0               268.1               -0.5774
   4500.0               243.0               -0.6865
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                  RUN NO. 34  FEB. 23/76

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                               0.350
  POTASSIUM AMIDE                                             0.480
SYSTEM TEMPERATURE (DEG C)                               [illegible]6.1

TOTAL INITIAL PRESSURE (ATM)                                  1.878
GAS VOLUME (CC)                                               2521.4
INTERFACIAL AREA (SQ.CM)                                      46.07
MONOMETHYLAMINE DENSITY (G/CC)                                0.7289

LIQUID FLOWRATE (CC/SEC)                                      0.234
GAS FLOWRATE (CC/SEC)                                         50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                   8823.4
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                              0.756E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                     23.8
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                  130.3
MOLE FRACTION HYDROGEN IN GAS PHASE                           0.886
MOLE FRACTION AMINE IN GAS PHASE                              0.114

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                    0.3575
VISCOSITY OF HYDROGEN GAS (CP)                                0.00762
VISCOSITY OF AMINE VAPOR (CP)                                 0.00644
VISCOSITY OF GAS MIXTURE (CP)                                 0.00793

DENSITY OF GAS PHASE (G/CC)                                   0.00051
GAS PHASE REYNOLD'S NUMBER                                    27.0
OVERALL LIQUID PHASE TRANSFER                                 0.0889*
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                           0.3924
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                    0.0899
FIRST ORDER RATE CONSTANT (1/SEC)                             106.9


   TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
   (SEC)         CONCENTRATION (PPM)
     0.0                475.3                0.0000
   600.0                455.9               -0.0438
  1300.0                432.0               -0.1008
  2100.0                399.3               -0.1842
  3000.0                375.5               -0.2496
  4000.0                347.4               -0.3331
  5000.0                321.3               -0.4171
  6000.0                297.0               -0.5023
  7000.0                275.5               -0.5841
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                 RUN NO. 35  FEB. 27/76

 CATALYST CONCENTRATION (M EQ/G)
   LITHIUM AMIDE                                              0.350
   POTASSIUM AMIDE                                            0.480
 SYSTEM TEMPERATURE (DEG C)                                   -13.1

 TOTAL INITIAL PRESSURE (ATM)                                 2.059
 GAS VOLUME (CC)                                              2522.2
 INTERFACIAL AREA (SQ.CM)                                     46.05
 MONOMETHYLAMINE DENSITY (G/CC)                               0.7029

 LIQUID FLOWRATE (CC/SEC)                                     0.267
 GAS FLOWRATE (CC/SEC)                                        50.2
 HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  6726.0
 HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.109E-03

 GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    28.0
 LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 131.3
 MOLE FRACTION HYDROGEN IN GAS PHASE                          0.644
 MOLE FRACTION AMINE IN GAS PHASE                             0.356

 DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.2875
 VISCOSITY OF HYDROGEN GAS (CP)                               0.00813
 VISCOSITY OF AMINE VAPOR (CP)                                0.00709
 VISCOSITY OF GAS MIXTURE (CP)                                0.00814

 DENSITY OF GAS PHASE (G/CC)                                  0.00119
 GAS PHASE REYNOLD'S NUMBER                                   61.1
 OVERALL LIQUID PHASE TRANSFER                                0.1964
   COEFFICIENT (CM/SEC)

 GAS PHASE MASS TRANSFER COEFFICIENT                          0.3536
   (G MOLE/(SEC SQ.CM(G MOLE/CC)))
 LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.2045
 FIRST ORDER RATE CONSTANT (1/SEC)                            381.2


    TIME         GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
    (SEC)        CONCENTRATION (PPM)
      0.0             445.5                  0.0000
    600.0             388.0                 -0.1483
   1200.0             336.9                 -0.3013
   1800.0             294.3                 -0.4497
   2400.0             254.3                 -0.6126
   3600.0             193.0                 -0.9281
   4800.0             150.3                 -1.2281
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                    RUN NO. 36  MAR. 09/76

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                              0.250
  POTASSIUM AMIDE                                            0.500
SYSTEM TEMPERATURE (DEG C)                                   -48.3

TOTAL INITIAL PRESSURE (ATM)                                 1.768
GAS VOLUME (CC)                                              2536.8
INTERFACIAL AREA (SQ.CM)                                     46.07
MONOMETHYLAMINE DENSITY (G/CC)                               0.7419

LIQUID FLOWRATE (CC/SEC)                                     0.201
GAS FLOWRATE (CC/SEC)                                        50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  10246.0
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.602E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    20.0
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 130.6
MOLE FRACTION HYDROGEN IN GAS PHASE                          0.944
MOLE FRACTION AMINE IN GAS PHASE                             0.056

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.3788
VISCOSITY OF HYDROGEN GAS (CP)                               0.00735
VISCOSITY OF AMINE VAPOR (CP)                                0.00610
VISCOSITY OF GAS MIXTURE (CP)                                0.00758

DENSITY OF GAS PHASE (G/CC)                                  0.00034
GAS PHASE REYNOLD'S NUMBER                                   19.2
OVERALL LIQUID PHASE TRANSFER                                0.0610
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                          0.3998
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.0614
FIRST ORDER RATE CONSTANT (1/SEC)                            62.5


    TIME         GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
   (SEC)         CONCENTRATION (PPM)
     0.0               496.7                 0.0000
   600.0               482.4                -0.0305
  1300.0               468.5                -0.0609
  2000.0               447.7                -0.1084
  3000.0               431.3                -0.1474
  4000.0               408.6                -0.2044
  5000.0               396.1                -0.2369
  6000.0               377.5                -0.2876
  7000.0               361.0                -0.3350
```

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                    RUN NO. 37  MAR. 12/76

    CATALYST CONCENTRATION (M EQ/G)
      LITHIUM AMIDE                                          0.250
      POTASSIUM AMIDE                                        0.500
    SYSTEM TEMPERATURE (DEG C)                              -12.2

    TOTAL INITIAL PRESSURE (ATM)                             2.128
    GAS VOLUME (CC)                                          2550.6
    INTERFACIAL AREA (SQ.CM)                                 46.05
    MONOMETHYLAMINE DENSITY (G/CC)                           0.7019

    LIQUID FLOWRATE (CC/SEC)                                 0.287
    GAS FLOWRATE (CC/SEC)                                    50.2
    HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)              6660.2
    HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                         0.111E-03

    GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                28.1
    LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)             131.1
    MOLE FRACTION HYDROGEN IN GAS PHASE                      0.641
    MOLE FRACTION AMINE IN GAS PHASE                         0.359

    DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)               0.2789
    VISCOSITY OF HYDROGEN GAS (CP)                           0.00815
    VISCOSITY OF AMINE VAPOR (CP)                            0.00712
    VISCOSITY OF GAS MIXTURE (CP)                            0.00816

    DENSITY OF GAS PHASE (G/CC)                              0.00123
    GAS PHASE REYNOLD'S NUMBER                               63.3
    OVERALL LIQUID PHASE TRANSFER                            0.2130
      COEFFICIENT (CM/SEC)

    GAS PHASE MASS TRANSFER COEFFICIENT                      0.3463
      (G MOLE/(SEC SQ.CM(G MOLE/CC)))
    LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)               0.2229
    FIRST ORDER RATE CONSTANT (1/SEC)                        447.1


      TIME          GAS PHASE DEUTERIUM    LN((Y-YE)/(YI-YE))
      (SEC)         CONCENTRATION (PPM)
        0.0               445.9                 0.0000
      600.0               383.0                -0.1631
     1200.0               324.1                -0.3446
     1800.0               278.3                -0.5127
     2400.0               243.4                -0.6630
```

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                RUN NO. 38  MAR. 17/76

CATALYST CONCENTRATION (M EQ/G)
  LITHIUM AMIDE                                              0.250
  POTASSIUM AMIDE                                            0.500
SYSTEM TEMPERATURE (DEG C)                                  -22.6

TOTAL INITIAL PRESSURE (ATM)                                 2.082
GAS VOLUME (CC)                                              2535.8
INTERFACIAL AREA (SQ.CM)                                     46.05
MONOMETHYLAMINE DENSITY (G/CC)                               0.7138

LIQUID FLOWRATE (CC/SEC)                                     0.241
GAS FLOWRATE (CC/SEC)                                        50.2
HENRY'S LAW COEFFICIENT (ATM/MOLE FRACTION)                  7507.2
HD-AMINE DIFFUSIVITY (SQ.CM/SEC)                             0.948E-04

GAS PHASE EQUILIBRIUM CONCENTRATION (PPM)                    26.0
LIQUID PHASE EQUILIBRIUM CONCENTRATION (PPM)                 132.1
MOLE FRACTION HYDROGEN IN GAS PHASE                          0.782
MOLE FRACTION AMINE IN GAS PHASE                             0.218

DIFFUSIVITY OF HD IN GAS PHASE (SQ.CM/SEC)                   0.3091
VISCOSITY OF HYDROGEN GAS (CP)                               0.00792
VISCOSITY OF AMINE VAPOR (CP)                                0.00682
VISCOSITY OF GAS MIXTURE (CP)                                0.00816

DENSITY OF GAS PHASE (G/CC)                                  0.00084
GAS PHASE REYNOLD'S NUMBER                                   43.2
OVERALL LIQUID PHASE TRANSFER                                0.1670
  COEFFICIENT (CM/SEC)

GAS PHASE MASS TRANSFER COEFFICIENT                          0.3632
  (G MOLE/(SEC SQ.CM(G MOLE/CC)))
LIQUID PHASE TRANSFER COEFFICIENT (CM/SEC)                   0.1719
FIRST ORDER RATE CONSTANT (1/SEC)                            311.5


   TIME        GAS PHASE DEUTERIUM   LN((Y-YE)/(YI-YE))
  (SEC)        CONCENTRATION (PPM)
     0.0              448.2               0.0000
   600.0              396.0              -0.1321
  1800.0              318.8              -0.3659
  2400.0              291.0              -0.4655
  3000.0              257.4              -0.6012
  3600.0              238.6              -0.6861
  4800.0              193.5              -0.9246
```

APPENDIX D

DETAILED ANALYSIS OF AMINOMETHANE SOLUTIONS FOR CATALYST CONCENTRATIONS

Concentration of PMA used = 0.31 m mol/g amine

Date of analysis: July 30, 1974

Sample appearance: Clear, light brown, no precipitate

Analytical method	a.a.s.	n.m.r.
Concentration found	(m eq/g)	(m eq/g)
K^+	0.42	
CH_3NH^-		0.31
$CH_3N\text{-}CH{=}N\text{-}CH_3^-$		0.09

Comments: G.C. analysis showed a small amount of KNH_2 in solution and 0.6% by weight dimethylamine in the solvent.

Concentration of PMA used = 0.30 m mol/g amine

Concentration of LMA used = 0.30 m mol/g amine

Date of analysis: October 2, 1974

Sample appearance: Dark color, contained precipitate

Analytical method	a.a.s.	n.m.r.	g.c.	a.a.s. on Filtered Sample
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.35			0.28
Li^+	0.33			0.26
NH_2^-			0.08	
CH_3NH^-		0.68	0.70	

Comments: Analyzed samples were cloudy. Variations in the results may be due to precipitate in the samples.

Date of analysis: October 23, 1974

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.34		
Li^+	0.37		
NH_2^-		0.07	
CH_3NH^-		0.69	0.73
$CH_3N\text{-}CH{=}N\text{-}CH_3^-$		nil	nil

Comments: Contains ≈ 10% NH_3 as the metal salt. The solvent does not contain a detectable amount of free ammonia.

Date of analysis: March 26, 1975

Sample appearance: Clear, pale yellow

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.32		
Li^+	0.32		
NH_2^-			0.04
CH_3NH^-		0.59	0.62
$CH_3N\text{-}CH{=}N\text{-}CH_3^-$		trace	0.004

Concentration of PMA used = 0.43 m mol/g amine

Concentration of LMA used = 0.43 m mol/g amine

Date of analysis: April 15, 1975

Sample appearance: Clear yellow solution

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.46		
Li^+	0.48		
NH_2^-			0.08
CH_3NH^-		0.94	0.90
$CH_3N-CH=N-CH_3^-$		trace	0.004

Date of analysis: May 5, 1975

Sample appearance: Clear, yellow

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(n eq/g)	(m eq/g)
K^+	0.44		
Li^+	0.46		
NH_2^-			0.06
CH_3NH^-		0.82	0.83
$CH_3N-CH=N-CH_3^-$		0.07	-

Concentration of PMA used = 0.63 m mol/g amine

Concentration of LMA used = 0.63 m mol/g amine

Date of analysis: May 13, 1975

Sample appearance: Clear, yellow

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.69		
Li^+	0.68		
NH_2^-			0.11
CH_3NH^-		1.36	1.32
$CH_3N-CH=N-CH_3^-$		0.05	-

Date of analysis: July 29, 1975

Sample appearance: Clear, bright yellow

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.66		
Li^+	0.66		
NH_2^-		-	0.10
CH_3NH^-		[illegible]23	1.14
$CH_3N-CH=N-CH_3^-$		trace	0.02

Concentration of PMA used = 0.39 m mol/g amine

Concentration of LMA used = 1.66 m mol/g amine

Date of analysis: June 6, 1975

Sample appearance: Pale yellow, slightly cloudy

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.40		
Li^+	1.67		
NH_2^-			nil
$CH_3NH_2^-$		2.04	2.03
$CH_3N-CH=N-CH_3^-$		nil	nil

Date of analysis: August 11, 1975

Sample appearance: Clear, nearly colorless

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.38		
Li^+	1.64		
NH_2^-			0.04
CH_3NH^-		2.12	2.09
$CH_3N-CH=N-CH_3^-$		nil	nil

Concentration of PMA used = 0.40 m mol/g amine

Date of analysis: September 8, 1975

Sample appearance: Clear, yellow solution

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.446		
Li^+	–		
NH_2^-		–	0.007
CH_3NH^-		0.425	0.422
CH_3N-[illegible]-N-CH_3^-		–	–

Date of analysis: October 9, 1975

Sample appearance: Clear, yellow

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.41		
NH_2^-		–	0.006
CH_3NH^-		0.376	0.371
$CH_3N-CH=N-CH_3^-$		0.016	0.004

Concentration of PMA used = 0.50 m mol/g amine

Concentration of LMA used = 0.86 m mol/g amine

Date of analysis: November 7, 1975

Sample appearance: Clear, yellow

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	[illegible] eq/g)
K^+	0.51		
Li^+	0.876		
NH_2^-		–	0.004
CH_3NH^-		1.363	1.164
$CH_3N\text{-}CH{=}N\text{-}CH_3^-$		–	–

Concentration of PMA used = 0.48 m mol/g amine

Concentration of LMA used = 0.35 m mol/g amine

Date of analysis: February 18, 1976

Sample appearance: Clear, yellow

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.50		
Li^+	0.374		
NH_2^-		–	0.0244
CH_3NH^-		0.8375	0.8080
$CH_3N{-}CH{=}N{-}CH_3^-$		0.0327	0.0081

Concentration of PMA used = 0.50 m mol/g amine

Concentration of LMA used = 0.25 m mol/g amine

Date of analysis: April 6, 1976

Sample appearance: Clear, yellow-gold

Analytical method	a.a.s.	n.m.r.	g.c.
Concentration found	(m eq/g)	(m eq/g)	(m eq/g)
K^+	0.5020		
Li^+	0.2553		
NH_2^-		-	0.0258
CH_3NH^-		0.7563	0.627
$CH_3N\text{-}CH{=}N\text{-}CH_3^-$		0.0272	0.006

END

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FIN

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