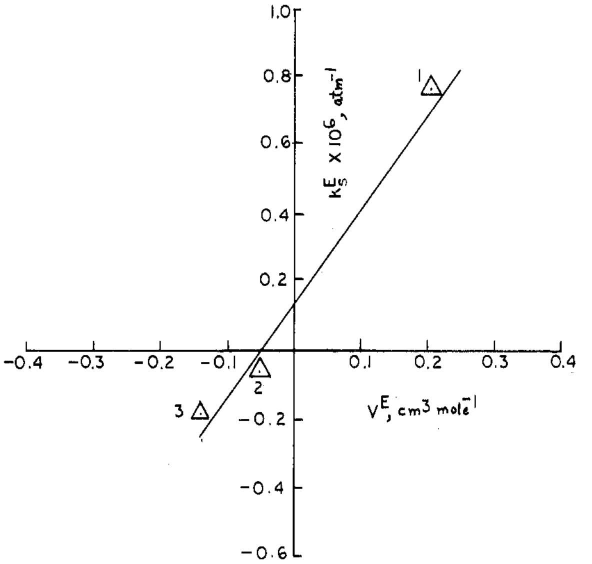


Figure 3. Plot of k_s^E vs. V^E for equimolal mixtures at 303.15 K: (1) C_2HCl_3–benzene; (2) C_2HCl_3–toluene; (3) C_2HCl_3–p-xylene.

attributed to the increased π-electron density of the aromatic molecule which will act as a π-type sacrificial electron donor toward C_2HCl_3. The possibility of formation of donor–acceptor complexes due to hydrogen bonding between $CHCl_3$ and C_2HCl_3 and due to σ–π interaction between CCl_4 and C_2HCl_3 has been indicated.

Acknowledgment. We are grateful to Professor R. P. Rastogi, Head of the Chemistry Department, Gorakhpur University, for encouragement during the present investigation. Thanks are also due to the University Grants Commission, New Delhi, for financial support.

References and Notes

(1) Currently with Chemistry Department, N. D. College, Barhalganj, Gorakhpur.
(2) J. Nath and S. N. Dubey, *J. Chem. Thermodyn.*, **11**, 1163 (1979).
(3) J. Nath and S. N. Dubey, *J. Chem. Thermodyn.*, in press.
(4) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).
(5) R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **61**, 2102 (1965).
(6) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, Amsterdam, 1950.
(7) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Technique of Organic Chemistry", Vol. VII, Interscience, New York, 1955.
(8) R. P. Rastogi and J. Nath, *Indian J. Chem.*, **5**, 249 (1967).
(9) K. S. Reddy and P. R. Naidu, *J. Chem. Thermodyn.*, **8**, 1208 (1976).
(10) T. B. Hoover, *J. Phys. Chem.*, **73**, 57 (1969).
(11) N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Behaviour", Van Nostrand-Reinhold, London, 1969, p 31.
(12) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, 1963.
(13) See ref 11, p 30.
(14) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).
(15) R. Thacker and J. S. Rowlinson, *J. Chem. Phys.*, **21**, 2242 (1953).
(16) K. C. Reddy, S. V. Subrahmanyam, and J. Bhimasenachar, *Trans. Faraday Soc.*, **58**, 2352 (1962).

Methylamine–Deuterium Isotope Exchange Equilibria in the Gaseous and Liquid Phases

J. H. Rolston,* J. den Hartog, J. P. Butler,

Atomic Energy of Canada Limited, Research Company, Chalk River Nuclear Laboratories, Physical Chemistry Branch, Chalk River, Ontario K0J 1J0, Canada

L. Silberring, and Hs. H. Günthard

Physical Chemistry Laboratory, Swiss Federal Institute of Technology, ETHZ-Zentrum, 8092 Zürich, Switzerland

(Received: September 10, 1979; In Final Form: March 7, 1980)

Publication costs assisted by Atomic Energy of Canada Limited and Swiss Federal Institute of Technology

The deuterium–protium separation factor, α, between molecular hydrogen and liquid methylamine in the presence of potassium methylamide catalyst has been measured at low deuterium concentrations over the temperature range −50 to +5 °C. The separation factor is about 10% larger than that for liquid ammonia, and its dependence upon absolute temperature, T, is given by $\ln \alpha = 0.1135 + (240.05/T) + (43989/T^2)$. The equilibrium constant, K_1, for deuterium–protium exchange between hydrogen and the amino group of methylamine vapor has been calculated for all deuterium concentrations at temperatures between 150 and 400 K with partition functions for methylamine derived from an internal rotation–inversion–normal vibration model of methylamine based on spectroscopic data. Conversion of K_1 into α values, by inclusion of vapor–liquid fractionation effects, shows that the discrepancy between theory and experiment is less than the combined tolerances (±5%) of the two approaches. The dependence of α on deuterium atom fraction is discussed.

1. Introduction

A precise determination of the overall deuterium–protium separation factor, α, between hydrogen and liquid methylamine is required to critically evaluate the economics of a proposed bithermal process for the extraction of deuterium from hydrogen streams.[1,2] The magnitude of α is primarily governed by the equilibrium isotope effect on the deuterium distribution between hydrogen and the amino group of methylamine vapor and to a lesser extent on the fractionation effect arising through the different volatilities of protio- and N-deuteriomethylamines.

At low deuterium concentrations the isotope distribution in the gas phase is governed by the equilibrium constant, K_1, for the exchange between methylamine vapor (v) and hydrogen gas (g) (eq 1).

$$CH_3NH_2(v) + HD(g) \rightleftharpoons CH_3NHD(v) + H_2(g) \qquad (1)$$

Values of K_1 have not previously been reported, in contrast to several experimental[3,4] and theoretical[5,6] studies of the corresponding equilibrium constant for exchange between hydrogen and liquid ammonia. A recent reevaluation of theoretical and experimental data shows that the equilibrium data may be considered reliably known within 2%.[7] Even better agreement has been noted for the corresponding equilibrium constant between hydrogen and water vapor[8] when a correction for deviations from the Born–Oppenheimer approximation is included.[9] Both of these studies involve exchange between hydrogen and relatively small molecules, where the required spectroscopic data can be extracted from well-characterized molecular potential functions. The absence of a correspondingly close theoretical analysis for molecules of even the modest complexity of methylamine led to the direct experimental approach described in the first half of the paper. Replacement of a proton of ammonia with a methyl substituent was not expected to change the equilibrium constant by more than a few percent since the free energy change governing eq 1 is primarily associated with the difference in the zero-point energies of the isotopic methylamines, substituted in the amino group, minus the difference in the isotopic hydrogen molecules. The experiments have been carried out in the temperature range -50 to +4 °C at a low atom fraction of deuterium, where only one atom of protium is replaced by deuterium in either molecule, while the proportion of molecules in which both atoms are replaced is negligible. Experimental results are compared with those corresponding to exchange between ammonia and hydrogen.

The second section of the paper deals with the statistical thermodynamics of methylamine and its deuterated modifications originating by replacement of any or both amino protons by deuterium. As a consequence, two ratios of partition functions are estimated, allowing one to calculate the internal equilibrium constant of the isotopic modifications of methylamine, as well as the deuterium separation factor between methylamine and hydrogen at any deuterium concentration.

The results of the experimental and statistical investigations described above are compared in the third section. In addition, a comparison is made with data for ammonia, which originate from a recent reassessment of most published experimental and statistical evidence related to the latter.

A method for calculating the multicomponent isotopic equilibria is described in the fourth section. The gas-phase separation factors, based on the statistical calculations of the equilibria, are tabulated over the mentioned temperature range and the full deuterium concentration range. The deuterium separation factor between liquid and gaseous methylamine is also tabulated on the basis of published experimental evidence. Some particulars of the statistical calculations are described in the Appendix.

2. Experimental Section

(*i*) *Procedure.* The flask used to equilibrate hydrogen and liquid methylamine was similar to that previously described.[8] Three separate series of experiments were conducted by using two concentration levels of deuterium in the amino group of liquid methylamine. For each series the potassium methylamide catalyst was prepared in advance by pressing under vacuum weighed amounts (40–130 mg) of potassium wire into the equilibration flask. This reacted with 5 mL of purified anhydrous methylamine at 0 °C in the presence of 1 cm^2 of electrolytically blackened platinum screen. All transfers, distillations, and solvent degassing procedures were carried out on a vacuum line. After 48-h reaction time the initial deep blue color of the solution was transformed to straw yellow. This solution was frozen and the hydrogen evolved during amide formation was pumped off. The flask was warmed to room temperature, and unreacted methylamine was transferred to a trap cooled in liquid nitrogen. A total of 0.114 mol of deuterium-enriched liquid methylamine (atom fraction, $x = 29\,000 \times 10^{-6}$) was transferred at 23 °C from a calibrated storage bulb into the reaction vessel. The liquid was stirred at room temperature to dissolve the potassium methylamide and was refrozen before introducing a measured quantity of deuterium gas (enriched hydrogen gas atom fraction $y = 9614 \times 10^{-6}$). The sample cell was immersed in the constant-temperature bath at -40 °C and allowed to reach equilibrium. The liquid methylamine was gently agitated by an externally mounted magnet. Following 30 min for thermal equilibration, gas samples were withdrawn through the pinhole valve at intervals of 30 min and were expanded through a liquid-nitrogen-cooled trap directly into the Consolidated Electronics CEC 21-614 mass spectrometer for isotope analysis. Repetitive samples taken over several hours showed no variation with time, indicating that both thermal and isotopic equilibria had been achieved and were maintained. Temperatures were measured on calibrated thermometers to within 0.01 °C, and a given series of measurements spanning a range of temperatures was completed within 12 h of the contacting of the deuterated methylamine with the potassium methylamide catalyst. No significant exchange of deuterium with the methyl group is expected under these conditions.[10]

(*ii*) *Standards.* In order to obtain deuterium analyses of the samples of hydrogen extracted from the equilibration cell, it was necessary to measure the sensitivity factors of the spectrometer for both H_2 and HD species.[8] A series of standards spanning a range of deuterium concentrations was prepared by equilibrating hydrogen of natural isotopic abundance with large quantities of isotopically enriched liquid water ($x = 5000 \times 10^{-6}$–$20\,000 \times 10^{-6}$) in a gas–liquid contacting column packed with wetproofed platinum catalyst spheres.[11] Hydrogen gas was recirculated for several hours at a constant column temperature while fresh liquid water was trickled once down the column. Deuterium-enriched water was prepared by weight dilution of D_2O (99.80 wt %) with water of natural isotopic abundance ($x = 146 \times 10^{-6}$). When either the deuterium content of the liquid feed or the temperature of the column was varied, hydrogen standards of varying contents could be prepared. The deuterium concentrations of these standards, expressed in terms of the deuterium-to-protium atom ratio, were calculated from the known separation factor and the calculated atom ratio of the feed water. An allowance for the H_3^+ contribution to the mass 3 peak was made as previously described.[8]

(*iii*) *Isotopic Analysis of Methylamine.* Two independent methods were used to confirm the initial deuterium atom fractions, x^i, of the stock samples of liquid methylamine used in these experiments.

Method A. Ignition of methylamine vapor and oxygen[12] in the mole ratio 1.14 to 1.00 results in a relatively simple reaction which can be represented by eq 2. Test samples

$$O_2 + 2CH_3NH_2 \rightarrow 2CO + N_2 + 5H_2 + 159\ \text{kJ} \quad (2)$$

of CH_3NH_2–O_2 mixtures at a total pressure of 40 kPa were ignited by means of a hot platinum wire in a 100-cm^3 Pyrex bulb. Mass analysis of the products on a CEC 21-610 mass spectrometer confirmed the general stoichiometry of eq 2 with 73% of the hydrogen of the methylamine appearing by hydrogen gas. Small amounts of HCN (4%), H_2O (2%), NH_3 (1%), and CO_2 (1%) were identified as gaseous side

TABLE I: Deuterium Analyses of Liquid Methylamine

	10^5 (deuterium atom fraction x)		
sample	calcd	method A (ignition)	method B (Schiff base)
CH_3NH_2[a]			143
CH_3ND_2[b] + CH_3NH_2[a]	29 153	29 140 ± 300	29 345 ± 550
run 1 stock[c]		27 785	
run 2 stock		28 275	28 650 ± 300
run 3 stock		44 273	44 098 ± 400
run 2 used[d]		28 795	29 297
run 3 used		43 979	44 343

[a] Natural abundance. [b] Purchased from Merck Sharp and Dohme of Canada with 98 atom % D in the amino position. [c] Stock concentrations refer to initial atom fraction before contact with hydrogen. [d] Used samples were recovered from exchange cell after equilibrations were completed.

products, whereas formaldehyde, methane, or nitrogen oxides were less than 0.05% of the product mixtures. The combustion mixture was cooled with liquid nitrogen, and the deuterium content of the hydrogen was determined on the CEC 21-610 mass spectrometer. A separate test on a sample of hydrogen of known deuterium content in the presence of CO and nitrogen showed that no additional fractionation occurred in the analysis of such mixtures on this spectrometer.

Method B. Formation of a Schiff base between methylamine and benzaldehyde in anhydrous benzene with the elimination of water offers a specific method for analysis of the deuterium content of the amino group. Typically 10 cm^3 of freshly distilled benzaldehyde, free of benzoic acid, and 30 cm^3 of toluene, predried over metallic sodium, were transferred from reservoirs into a carefully dried 100-cm^3 distillation flask equipped with a condenser. A 2-cm^3 sample of chilled liquid methylamine was vaporized and bubbled into the reaction flask. The mixture was heated to boiling to decompose the Schiff base, and the water (65–75% of theory) was immediately collected as the azeotrope. The deuterium concentration of the water condensate was adjusted to less than 1 atom % by dilution with water of natural deuterium abundance. The optical density at 2500 cm^{-1} of a 0.25-mm thick sample in a CaF_2 cell, referenced against a matched cell containing natural water, was measured on a Perkin-Elmer Model 21 spectrometer.[13,14] The optical density difference, corrected for interference from residual methylamine, was compared against those of known water standards.

Results from both analytical methods for a standard sample of deuterated methylamine and for the stock solutions used in the α measurements are given in Table I. The good agreement between the two methods of analysis for solutions recovered from the equilibration flasks confirmed the absence of any transfer of deuterium between the methyl and amino groups.

(iv) Calculations. The deuterium atom fraction present in the liquid phase at equilibrium, x^e, was calculated for each temperature with the aid of a deuterium mass balance taken over the two phases present whereby

$$x^e = \frac{x^i(1 + S) + R(y^i - y^e)}{1 + S\alpha_v^{-1}} \tag{3}$$

The symbols x^i, y^i, and y^e refer to the initial (i) or equilibrium (e) deuterium atom fractions present in the liquid and hydrogen, respectively. The mole ratio of initially added hydrogen to liquid methylamine at equilibrium is denoted by R, and S is the mole ratio of vapor to liquid at equilibrium. The separation factor, α_v between methylamine vapor and liquid is defined in terms of the respective deuterium atom fractions x^e and z^e by eq 4.

TABLE II: Temperature Dependence of Separation Factor α

	deuterium atom fractions		
temp, °C	$10^6 y^e$	$10^6 x^e$	separation factor, α
-0.40	5771	28 213	5.002
-0.40	5747	28 213	5.023
-0.40	5816	28 213	4.963
-35.40	4264	27 486	6.600
-35.40	4242	27 485	6.634
-35.40	4179	27 486	6.735
-50.00	5850	44 015	7.824
-50.00	5779	44 015	7.921
-50.00	5859	44 015	7.812

$$\alpha_v = \frac{x^e(1 - z^e)}{z^e(1 - x^e)} \tag{4}$$

When eq 3 is derived for the low deuterium concentrations used in this study, α_v can be equated, without significant error, to the ratio x^e/z^e. Examination of this equation shows that x^e is essentially equal to x^i plus a small correction which, for the concentrations used herein, approaches 0.2% when the molar ratios of hydrogen and amine vapor to liquid methylamine are 0.008 and 0.0002, respectively.

2.1. Results. The atom fraction of deuterium, x^e, present in the liquid at equilibrium at each temperature was calculated from eq 3. Corrections were made for the lowering of the vapor pressure by the potassium methylamide catalyst and for the isotopic dilution of the stock solutions due to the protium content of the preformed amide catalyst. The amount of hydrogen dissolved in methylamine at all temperatures was less than 1% of the total hydrogen in the cell so that the equilibrium mole ratio of dissolved hydrogen to liquid did not exceed 1.5×10^{-4}. As noted with liquid water, neglect of the dissolved hydrogen does not alter the calculated equilibrium concentrations of the liquid amine by more than 10^{-3}%. Representative results from the three stock solutions given in Table I are listed in Table II. (See paragraph at end of text regarding supplementary material.) These data were fitted to a weighted nonlinear least-squares regression for one dependent variable[15] to eq 5, in which T is the absolute

$$\ln \alpha = 0.1135 + \frac{240.05}{T} + \frac{43989}{T^2} \tag{5}$$

temperature. Weights for the dependent variables ln α were set equal to α_i^2 divided by an estimate of the variances of the measured α_i. This was assumed to be constant through the range of temperatures studied and was taken as the average standard deviation (0.06 for all of the measured α_i). The standard deviation in ln α obtained from the residual variance in the weighted least-squares fitting of eq 5 is 0.018, which corresponds to a 1.8% error in α over this range of temperatures. This is comparable to the error estimate of 1.5% for the separation factor between hydrogen and liquid water.[8] A comparison (Figure 1) of the separation factor for methylamine–HD with that for the liquid ammonia–HD system[4] shows that the separation factor for methylamine is significantly larger and is slightly more strongly dependent on temperature in this range. Values of the equilibrium constant K_1 can also be extracted from measurements of the overall separation factor α between hydrogen and liquid methylamine if allowance is made for vapor–liquid fractionation. The necessary fractionation factors, α_v, for temperatures be-

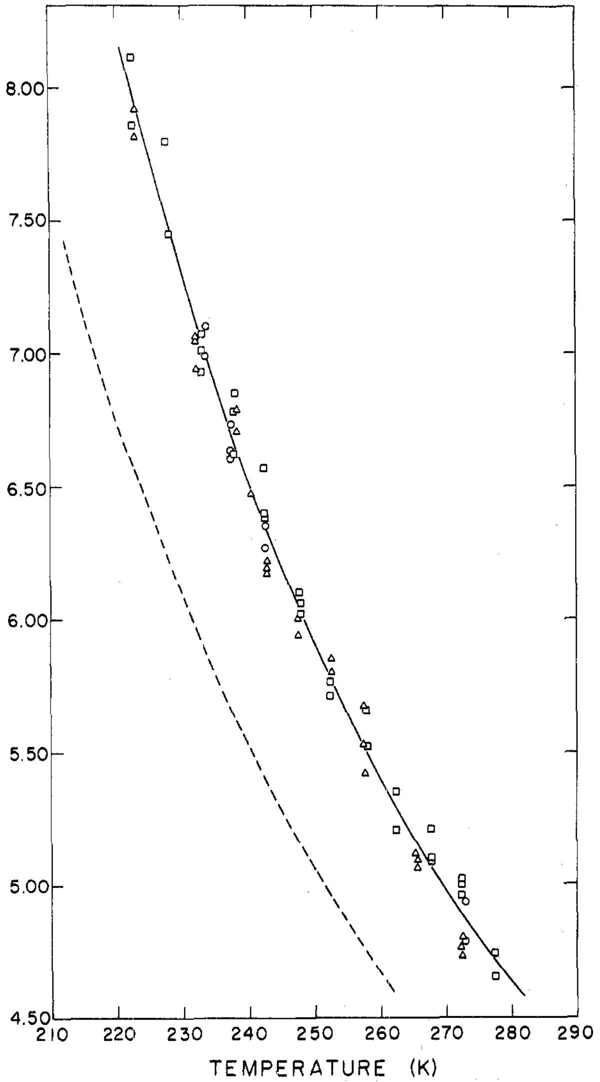


Figure 1. Temperature dependence of separation factors between molecular hydrogen and liquid ammonia (dashed line) data from ref 8, and liquid methylamine (solid line) data from run 1 (O), run 2 (Δ), and run 3 (□).

tween −55 and +20 °C were obtained by applying the relation

$$\alpha_v = (P_{CH_3NH_2}/P_{CH_3ND_2})^{0.500} \qquad (6)$$

to the data of Wolff and co-workers.[16-20] This relationship is derived from the rule of the geometric mean[21] formulated from the suggestion of Lewis and Cornish[22] that the vapor pressure of a molecule containing a mixture of isotopes such as CH_3NHD could be calculated as the square root of the product of the vapor pressures of the appropriate protio- and *N*-deuteriomethylamines. Application of the larger exponent of 0.524, suggested by Van Hook et al.[23] for the vapor pressure isotope effect of water species, gives values of α_v which are higher by about 0.3% over the temperature range considered. This discrepancy is within the uncertainties in the vapor pressure data of Wolff and co-workers, and hence the square root relationship has been adopted. Values of the vapor–liquid separation factor for temperatures between −55 and +20 °C were calculated from the vapor pressure of methylamine[16,17] and the averaged vapor pressure differences of protio and *N*-deuteriomethylamine.[17-20] In order to extend the temperature range it was assumed that $\alpha_v = 1$ at the critical point of methylamine (157 °C).

The combined data were fitted by a weighted least-squares regression to eq 7.

$$\ln \alpha_v = 0.00318 - \frac{14.27}{T} + \frac{5550}{T^2} \qquad (7)$$

Since both hydrogen and the amino group contain two exchangeable protons, the equilibrium constant K_1 governing exchange between hydrogen and methylamine vapor at low deuterium concentrations is equal to α/α_v. Values of K_1 were calculated by dividing the experimental α values by the appropriate value of α_v obtained from eq 7. These were fitted to eq 8. Values calculated from eq 8 differ by

$$\ln K_1 = 0.11447 + \frac{251.80}{T} + \frac{38798}{T^2} \qquad (8)$$

less than 0.02% from those obtained by subtraction of eq 5 and 7 over the temperature range −50 to +5 °C.

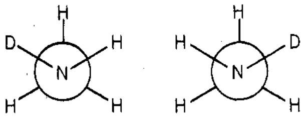
3. Statistical Thermodynamics

The thermodynamic treatment of the methylamine–hydrogen isotopic equilibria can be defined by eq 1, and the following two equations

$$CH_3NH_2(v) + CH_3ND_2(v) \rightleftharpoons 2CH_3NHD(v) \qquad (9)$$

$$H_2(g) + D_2(g) \rightleftharpoons 2HD(g) \qquad (10)$$

The molecule CH_3NHD exists in two stereoisomeric forms:



with identical thermodynamic properties. In the following sections the ratios of the partition functions Q_0, $Q_{1\pm}$, and Q_2 of CH_3NH_2, CH_3NHD, and CH_3ND_2, respectively, are calculated. Q_{1+} and Q_{1-} denote the partition functions of either one of the two optical antipodes. Later on the quantity $Q_1 = Q_{1+} + Q_{1-}$ is used for the calculation of the isotopic equilibria.

3.1. Partition Functions of the N-Deuteriomethylamines. A number of assumptions have been made for the calculation of the partition functions of the *N*-deuteriomethylamines.

(i) The partition functions for the ideal gas state can be evaluated from molecular properties of isolated molecules.

(ii) Methylamine is a nonrigid molecule which may be described by a $C_{\infty h}$F C_{3v}T C_{2v}I semirigid model[24] with an isometric group D_6.

(iii) The methylamine molecule has 13 (infinitesimal) vibrational degrees of freedom and 2 finite degrees of freedom. These correspond to inversion of the amino group and internal rotation of the methyl group.

(iv) The molecular partition function can be approximated by factorization into contributions from particular degrees of freedom (eq 11) where the indices t, r, v, inv,

$$Q = Q_t Q_r Q_v Q_{inv} Q_{inro} \qquad (11)$$

and inro denote translational (3), rotational (3), and vibrational (13) degrees of freedom, and the finite degrees NH_2 inversion and CH_3 internal rotation, respectively.

As a consequence the kinetic energy function was approximated to first order as a sum of a translational term, a vibrational term, and a term originating from overall rotation, inversion and internal rotation. The potential function for inversion (inversion angle τ) and internal rotation (internal rotation angle γ) has to be symmetric with respect to isometric substitutions[24]

$$\begin{bmatrix} \tau' \\ \upsilon' \\ 1 \end{bmatrix} = \begin{bmatrix} -1 & . & 0 \\ \cdot & 1 & \pi \\ . & . & 1 \end{bmatrix} \cdot \begin{bmatrix} \tau \\ \upsilon \\ 1 \end{bmatrix} \quad \begin{bmatrix} \tau' \\ \upsilon' \\ 1 \end{bmatrix} = \begin{bmatrix} 1 & . & . \\ . & 1 & 2\pi/3 \\ . & . & 1 \end{bmatrix} \cdot \begin{bmatrix} \tau \\ \upsilon \\ 1 \end{bmatrix} \qquad (12)$$

$$V(\tau,\upsilon) = V(-\tau,\upsilon-\pi) = V(\tau,\upsilon+2\pi/3) \qquad (13)$$

Thus the potential barrier for the CH_3 internal rotation depends on the inversion angle τ and the NH_2 inversion potential depends on υ. Qualitative discussion of the potential function has been presented by Tsuboi et al.,[25] and ab initio quantum chemical calculations have been carried out by T. K. Ha.[26] However, experimentally derived potential functions[27,28] are based on the form

$$V(\tau,\upsilon) \approx V(\tau) + (V_3/2)(1 - \cos 3\upsilon) \qquad (14)$$

which, in view of eq 13 cannot be correct.

Since the coefficients of the matrix of the kinetic energy expression depend on τ (for the rotation–inversion–internal rotation part) and on τ and υ for the vibrational energy part, the factorization (eq 11) required further approximations:

(i) The factor Q_r was evaluated for the r_0 structure of the molecule, either from molecular structural data or from rotational constants of the ground state. This amounts to neglect of the dependence of the inertia tensor on the inversion angle and separation of overall rotation and finite internal motion.

(ii) The partition function for inversion Q_{inv} was approximated by

$$Q_{inv} = \sum g_{\Gamma_j N}^{inv} \exp\left(-E_{\Gamma_j N}^{inv}/kT\right) \qquad (15)$$

where $E_{\Gamma_j N}^{inv}$ and $g_{\Gamma_j N}^{inv}$ denote energy eigenvalues and statistical weights, respectively, of the inversion problem of the $C_{\infty\upsilon}F$ $C_{2\upsilon}I$ semirigid model.[27] The Hamiltonian for inversion $\hat{H}^{inv}$ was written as

$$\hat{H}^{inv} = {}^1\!/_2(\hat{p}_\tau + {}^1\!/_4(\hat{p}_\tau \ln g))g^{44}(\tau)(\hat{p}_\tau - {}^1\!/_4(\hat{p}_\tau \ln g)) + V(\tau) \qquad (16)$$

where

$$\hat{H}^{inv}\psi_{\Gamma_j N}^{inv} = E_{\Gamma_j N}^{inv}\psi_{\Gamma_j N}^{inv} \qquad (17)$$

For this model an exact solution based on infinite matrix diagonalization has been given, including a computer program for convenient numerical calculation.[27] Separation of the factor Q_{inv} involves neglect of the interaction that inversion makes with overall rotation and, more importantly, with internal rotation. This interaction occurs through both the kinetic coefficients and the potential function $V(\tau,\upsilon)$ discussed above (eq 13). It should be remarked that application of the procedure mentioned above[27] is possible only to the inversion mode of the CH_3NH_2 and CH_3ND_2 species. For the CH_3NHD modification no exact treatment is available, and the eigenvalues $E_{\Gamma_j N}^{inv}$ have to be determined by a perturbation type estimate. Since the inversion barrier is rather high Q_{inv} is approximated at low temperatures with acceptable accuracy by either the inversion model mentioned above or the harmonic approximation.

(iii) The partition function, Q_{inro}, was approximated by

$$Q_{inro} \approx \sum g_{\Gamma_j N}^{inro} \exp\left(-E_{\Gamma_j N}^{inro}/kT\right) \qquad (18)$$

The statistical weights $g_{\Gamma_j N}^{inro}$ and energy levels $E_{\Gamma_j N}^{inro}$ were given by the internal rotation problem.[28] The Hamiltonian was taken as

$$\hat{H}^{inro} = \bar{g}^{55}\hat{p}_\upsilon{}^2 + {}^1\!/_2(1 - \cos 3\upsilon) \qquad (19)$$

$$\hat{H}^{inro}\psi_{\Gamma_j N}^{inro} = E_{\Gamma_j N}^{inro}\psi_{\Gamma_j N}^{inro} \qquad (20)$$

Obviously this approximation involves neglect of the dependence of the kinetic coefficient $\bar{g}^{55}$ on the inversion angle τ, and the coupling of internal rotation with inversion through the potential function $V(\tau,\upsilon)$ (cf. eq 13). For numerical calculation the value $\bar{g}^{55} = \langle g^{55}(\tau)\rangle$, for the inversion ground state, was taken, and the internal rotation barrier derived from vibration–rotation spectra (see below) was applied.

TABLE III: Structural Data for Methylamine

parameter	1[a]	2[b]
r_0(CH) (R_{20}), Å	(1.093)[c]	1.0987
r_0(NH) (R_{10}), Å	1.011	1.0096
r_0(CN) (R_{30}), Å	1.474	1.4714
∠ (HCH) θ_0, deg	(109° 28′)	108.0
∠ (CNH), deg	112° 03′	110.27
∠ (HNH) $2\delta_0$, deg	105° 52′	107.15
ϵ (tilt angle), deg	3° 30′	

[a] References 37–39. [b] Reference 40. [c] Values in parenthesis: assumed.

(iv) The vibrational partition function over the remaining 13 vibrational modes was calculated in the harmonic approximation, i.e., for each degree of freedom

$$Q_v = \exp(-ch\tilde{\nu}/2kT)(1 - \exp(-ch\tilde{\nu}/kT))^{-1} \qquad (21)$$
$$= \text{ZPEF}(1 - \exp(-ch\tilde{\nu}/kT))^{-1}$$

where ZPEF is the zero-point energy term. In order to obtain an estimate of the errors introduced by the harmonic approximation, we have employed two versions. In the first, normal frequencies were used instead of fundamental frequencies for all vibrational modes. In the second, normal frequencies for all vibrational modes except the five light atom stretching modes (ν(NH/D), ν(CH)) were used. For the latter, normal frequencies and anharmonic constants were determined by Dennison's approximation from fundamental frequencies of corresponding group modes of pairs of isotopic species. The vibrational partition function for the stretching modes ν(NH), ν(CH), etc. were calculated from the well-known expression for the energy levels of the anharmonic oscillator. It should be noted that the zero-point energy calculated along these lines for reactions 1, 9, and 10 are not of the degree of precision as for reaction 10 since for the three methylamine species no sufficiently complete anharmonicity data are available. The procedures mentioned above tend to underestimate the exponential function of the zero-point energy difference, e.g., for $Z_{1t}Z_0$ by the factor exp $3ch\{(\tilde{\nu}_{01}x_e - \tilde{\nu}_{01}'x_e')/4kT\}$ where $\tilde{\nu}_{01}$, $\tilde{\nu}_{01}'$, x_e, and x_e' denote fundamental frequencies and anharmonicity coefficients of the ν(NH) and ν(ND) stretching modes, respectively. However, the presently available data do not warrant a reliable correction for anharmonicity.

(v) The treatment of the two finite internal degrees of freedom was based on data and procedures described in the Appendix.

3.2. Molecular Data. In this section the molecular data used in the partition function calculations are compiled. Molar masses of the three isotopic species d_0, d_1, and d_2 were taken as 31.0422, 32.0485, and 33.0548 g mol^{-1}, respectively.

Structural parameters of methylamine have been derived from microwave rotational data and are collected in Table III. The two sets may be considered as equal within the error limits since they have been derived essentially from rotational constants within the rigid rotor approximation. They nevertheless may serve as a basis for estimation of errors in the rotational and vibrational factors of the partition functions originating from structural errors.

Rotational constants and moments of inertia for the isotopic species of methylamine have been reported by several workers; some of the data have been collected in Table IV. For the purpose of this work the inertia tensors

TABLE IV: Rotational Parameters of Methylamine

	d_0	d_1	d_2
A_0, MHz	22 630.5		20 280.0[c]
B_0, MHz	21 708.72		18 791.93
C_0, MHz	10 314.43		7 726.76
I_a, amu Å^2	4.9012		6.5426[c]
I_b, amu Å^2	22.3385		24.9276
I_c, amu Å^2	23.2870		26.9015
I_a, amu Å^2 [a]	4.9012	5.6424	6.4875
I_b, amu Å^2	22.3313	23.6494	24.9168
I_c, amu Å^2	23.2752	25.1687	26.9301
g,[a,b] (amu Å^2)^3	2547.460	3358.508	4353.195[c]

[a] Calculated from structural data, ref 40; 1 amu Å = $(6.0225 \times 10^{39})^{-1}$ g cm^{-2}. [b] $g = I_aI_bI_c$, calculated from structural data. [c] Reference 40.

of the three species d_0, d_1, and d_2 were calculated from the available structural data given in Table III. One of the sets obtained in this way is also included in Table IV. It serves as a basis for estimation of errors introduced by the uncertainties of rotational constants and structural parameters into the rotational factor.

Vibrational data for the d_0 and d_2 species have been taken from Shimanouchi's tables.[29] For the modification d_1 only fragmentary experimental vibrational data are available.[30] Zerbi et al.[31] derived at 21 parameter approximate harmonic valence type force field from a normal coordinate analysis (NCA) of the vibrational spectra of the isotopic modifications d_0, N-d_2, C-d_3, d_5, and some species of dimethyl- and trimethylamine. In their NCA the large amplitude modes, NH_2 wagging and CH_3 torsion, were considered as harmonic, and the light atom stretching modes were not corrected for anharmonicity. In this work the NCA for the species d_0, d_2, C-d_3, and d_5 was repeated for testing purposes, and then the harmonic valence force field was used to calculate the normal frequencies of the d_1 species.

The NCA was based on Wilson's FG-matrix technique. For determination of the G matrix, the structural data collected in Table III were adopted, and the conformation with the CH_3 group staggered with respect to the NH_2 group was chosen. For calculation of the vibrational partition functions, the normal frequencies of the three species d_0, d_1, and d_2 produced by the NCA were used. As mentioned above in the calculation of ZPEF, either the normal frequencies or the fundamentals were inserted to obtain estimates for errors in the vibrational factors.

The vibrational data are listed in Table V. It should be mentioned that the harmonic approximation to the finite amino group inversion and methyl group internal rotation modes are included. The list furthermore shows that assignments of Shimanouchi of the NH_2 (ND_2, NHD) twisting modes have been revised according to the results of the NCA.

3.3. Partition Function Ratios. The ratios of the partition functions obtained by the procedure outlined above are collected in Table VI. In the temperature range considered, the systematic errors introduced by the various approximations discussed in section 3.1 cannot be estimated with certainty. The most serious source of error appears to originate from the factorization of the sum of states into rotational, inversion, and internal rotation factors and the effects of anharmonicity in the ZPEF.

Estimates of errors in the partition function ratios related to uncertainties in structural parameters, potential functions for finite modes, and vibrational frequencies were obtained by substitution of different molecular data sets. From such calculations we arrive at errors for the partition function ratio Q_1/Q_0 of ≤2% for $T < 300$ K and ≤5% for $T = 400$ K. For $T \leq 300$ K the errors in the harmonic approximation of Q_1/Q_0 and Q_2/Q_1 are within the same limits. From this result one may conclude that the partition function ratios are reliable enough for prediction of H–D exchange at low temperatures for ideal gas-phase equilibria.

3.4. Deuterium–Protium Equilibria in Hydrogen. The hydrogen molecule and its various isotopic and ortho–para species have been extensively investigated. The most complete compilation of the thermal properties of hydrogen has been reported by Woolley et al.[32] The last paper published on the subject is by Kosloff et al.[33] In this work the compilation by Woolley et al. has been used. Some assessment of the precision of the equilibria data calculated here is possible by using more recent information. The difference in zero-point energies of various isotopic species provides the most important contribution to the ratio of partition functions. The evolution of these energy differences is outlined in Table VII. The errors in these values are not likely to be greater than 1 cm^{-1}. The influence of such errors on the equilibrium constant of deuterium exchange with any substance is 0.6% at 250 K and less at higher temperature.

The ratios of the partition functions Q_{HD}/Q_{H2} and Q_{D2}/Q_{HD} have been calculated here by using the tabulated values of the free enthalpy function in ref 32. The calculations have been made for normal mixtures of the ortho and para species and for equilibrium mixtures at each

TABLE V: Vibrational Frequencies of Methylamines (cm^{-1})

	d_0			d_1			d_2	
mode[a]	obsd[b]	calcd[c]	mode	obsd[d]	calcd[e]	mode[a]	obsd[b]	calcd[c]
a′$\nu_s(NH_2)$	3361	3377	aν(NH)	3388	3409	a′$\nu_E(CH_3)$	2961	2964
$\nu_E(CH_3)$	2961	2964	$\nu(CH_3)$		2965	$\nu_s(CH_3)$	2817	2810
$\nu_s(CH_3)$	2820	2809	$\nu(CH_3)$		2964	$\nu_s(ND_2)$	2479	2456
$\delta_s(CH_3)$	1430	1426	$\nu(CH_3)$		2810	$\delta_E(CH_3)$	1468	1467
$\delta(NH_2)$	1623	1629	ν(ND)	2506	2496	$\delta_s(CH_3)$	1430	1428
$\delta_E(CH_3)$	1473	1466	$\delta(CH_3)$		1472	$\delta_s(ND_2)$	1234	1221
$\gamma_r(CH_3)$	1130	1131	$\delta(CH_3)$	1469	1470	$\gamma_r(CH_3)$	1117	1127
ν(CN)	1044	1046	δ(NHD)		1452	ν(CN)	997	999
$\gamma_w(NH_2)$	780	796	$\delta_s(CH_3)$		1421	$\gamma_w(ND_2)$	625	611
a″$\nu_{as}(NH_2)$	3427	3439	$\gamma_r(CH_3)$	1143	1155	$\nu_E(CH_3)$	2985	2965
$\nu_E(CH_3)$	2985	2965	$\gamma_r(CH_3)$		1128	a″$\nu_{as}(ND_2)$	2556	2537
$\delta_E(CH_3)$	1485	1470	ν(CN)	1032	1039	$\delta_E(CH_3)$	1485	1469
$\gamma_r(CH_3)$	1195	1192	γ_t(NHD)	878	911	$\gamma_r(CH_3)$	1187	1140
$\gamma_t(NH_2)$		1015	γ_w(NHD)	687	677	$\gamma_t(ND_2)$		787
$T(CH_3)$	268	270	$T(CH_3)$		241	$T(CH_3)$	228	223
$\Sigma\tilde{\nu}$em[f]	2.700E4				2.561E4			2.420E4

[a] Approximate mode description, cf. ref 31 and this work. [b] Reference 29. [c] Reference 31 and this work, normal coordinate analysis. [d] Reference 30. [e] This work, normal coordinate analysis. [f] Sum of normal frequencies.

TABLE VI: Partition Function Ratios of the Methylamines[a]

temp, K	Q_{1+}/Q_0	Q_2/Q_{1+}
150	950	1035
175	371	398
200	184	195
225	107	112
250	69.0	71.9
275	48.5	50.2
300	36.2	37.3
350	23.0	23.5
400	16.4	16.7

[a] For error limits see section 3.3.

TABLE VII: Differences in Zero-Point Energy (cm^{-1})

ref	H_2-HD	HD-D_2
41	287.1	341.9
32	288.6	344.4
42	288.8	343.4
43	289.3	343.4
44	288.9	344.1

TABLE VIII: Partition Functions of Equilibrium (e) and Normal (n) Hydrogen with Variable Number of Deuterium Atoms[a]

temp, K	HD/e-H_2	HD/n-H_2	HD/n-H_2	e-D_2/HD and n-D_2/HD	n-D_2/HD
	nuclear spin contribution to the entropy				
	incl	incl	excl	incl	excl
150	116.2	116.6	77.74	44.67	29.78
175	77.09	77.20	51.47	28.06	18.70
200	56.96	56.98	37.99	19.80	13.20
225	45.15	45.15	30.10	15.10	10.07
250	37.54	37.54	25.03	12.15	8.103
275	32.31	32.31	21.54	10.18	6.785
300	28.53	28.53	19.02	8.776	5.851
350	23.47	23.47	15.65	6.957	4.638
400	20.29	20.29	13.53	5.843	3.895

[a] The ratios of the partition functions of normal mixtures within the temperature range $200 < T \leqslant 400$ K can be approximated by the following Antoine equations: $Q_{HD}/Q_{n\text{-}H2} = 4.977 \exp(393.9/(T - 6.13))$ and $Q_{D2}/Q_{HD} = 1.1476 \exp(489.2/(T + 0.29))$ when the nuclear spin contributions are excluded.

temperature. The following formulas have been used for the latter case:

$$\frac{Q_{DH}}{Q_{eH2}} = \frac{\exp(-F^\circ_{HD}/RT)}{\exp(-F^\circ_{pH2}/RT) + \exp(-F^\circ_{oH2}/RT)} \quad (22)$$

$$\frac{Q_{eD2}}{Q_{HD}} = \frac{\exp(-F^\circ_{pD2}/RT) + \exp(-F^\circ_{oD2}/RT)}{\exp(-F^\circ_{HD}/RT)} \quad (23)$$

where F°/T are tabulated standard values of the free enthalpy functions (including zero-point energies E_0°/T) of HD and ortho or para species of H_2 and D_2 as indexed. The value of the gas constant $R = 1.98714$ cal/(mol K) has been taken here from the same reference (32).

The results of the calculations are represented in Table VIII. Nuclear spin contributions to the entropy, as well as the entropy increase due to the mixing of the ortho and para species, are included in the first two columns of tabulated data for H_2 and in the first column for D_2. However, these contributions are usually not included in the data of other molecules containing hydrogen. Therefore, an additional column without them has been added for normal mixtures of H_2 and D_2. The ratios of the partition functions are then $^2/_3$ times lower. Any significant differences between the values for the equilibrated and normal compositions appear only up to 200 K for protium and below 150 K for deuterium.

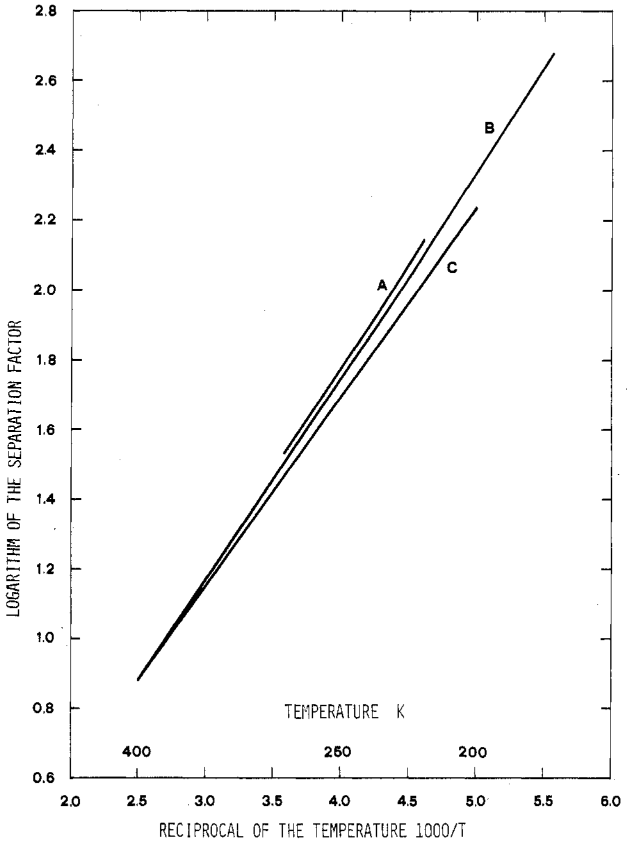


Figure 2. Comparison of separation factors between hydrogen and liquid methylamine (lines A and B) and liquid ammonia (line C) at low deuterium content: (A) experimental data this work eq 5; (B and C) statistical mechanical calculations of the gas-phase equilibria multiplied by measured data for the liquid-vapor equilibria.

For the purpose of this work a temperature range between 150 and 400 K has been considered. The temperature spacing of the tables of ref 32 is quite wide within this range. Care was taken in order to retain the precision of interpolated data. This was done by fitting the data to an Antoine equation, the coefficients of which have been estimated by a least-squares errors method for two temperature ranges, namely, 150–200 K and 200–400 K. The final close spaced partition function ratios, which are fully corrected for anharmonicity effects, are represented in Table XIII.

The ratios of the partition functions provide all information necessary for the estimation of the internal equilibria of an ideal gas mixture of isotopic species. The same is valid for external equilibria with any other gas for which the same information is available. The pressure effect on the gas-phase isotopic equilibria is negligible. Thus, even at relatively high pressure, the precision of the calculated separation factors remains high.

4. Comparison of Theory with Experiment

The results of measurements of the deuterium separation factor between liquid methylamine, liquid ammonia, and gaseous hydrogen at low atom fraction of deuterium are now compared with the results of calculations by statistical thermodynamics (Figure 2). The latter set of data covers a wider temperature range but includes experimental information from ref 18–20 about the liquid–vapor equilibria. This has been extrapolated below −55 °C and above 20 °C by using eq 7. The measured data have been taken from eq 5 for this comparison. The calculated curve

TABLE IX: Comparison of Deuterium-Protium Separation Factors

species	temp, K	
	220	280
liquid methylamine/H_2		
measured	8.28	4.63
calcd	7.90	4.44
liquid ammonia/H_2		
calcd	7.29	4.30

B for methylamine lies below the experimental curve A. Inclusion of anharmonicity corrections to the methylamine partition functions would tend to increase this discrepancy, but at present the required anharmonicity constants are considered insufficiently reliable to justify such a refinement. The difference is below 5% and can therefore be considered to be within the combined tolerances of both procedures.

Table IX shows that the separation factors for liquid ammonia and hydrogen are significantly below those of methylamine and hydrogen. The calculated ammonia-hydrogen data originate from a reassessment[7] of published information on the statistical thermodynamics of ammonia and a comparison with several published measurements of the gas-phase exchange as well as the liquid-vapor equilibria. In the temperature range considered, the reassessed value of the separation factors of the ammonia-hydrogen system are 6-8% higher than those given in ref 4.

5. Extension to High Concentrations

All information necessary for the calculation of the gas-phase isotopic equilibria is provided in section 3. For systems which include liquid phases, information on liquid-vapor equilibria is required.

5.1. Liquid-Vapor Methylamine-Deuterium Equilibria. The internal equilibria of the isotopic species in liquid methylamine are not easily accessible by theory. However, it is known that the liquid solutions of isotopic species are very nearly ideal and that the following relationship holds:

$$\frac{P_{j-1}}{P_j} = \alpha_v \tag{24}$$

where P_j designates the vapor pressure of a liquid component with j deuterium atoms and α_v is a temperature function independent of j. One conclusion from the above rule is that eq 6 holds. A second is that all internal equilibria of the liquid isotopic components are identical with those between vapor components containing the same number of deuterium atoms. In terms of the partition functions of liquid (L) and vapor (v) species this can be written as follows:

$$K_u(\mathrm{L}) = K_j(\mathrm{v}) \tag{25}$$

where

$$K_j = \frac{Q_j^2}{Q_{j+1}Q_{j-1}} \tag{26}$$

Equation 26 is not sufficient to solve the problem, but as soon as α_v, at low atom fraction of deuterium, is known (eq 7), all equilibria at any fraction are described.

5.2. Separation Factor at any Deuterium Level. Once all ratios of the partition functions of each involved substance are known, the molar proportion of any isotopic species at equilibrium can be found by any of the usual methods of treatment of multicomponent systems. Dealing with protium and deuterium in hydrogen and methylamine, there are five different molecules of hydrogen (including ortho-para modifications of H_2 and D_2) and three different molecules of methylamine. When deuterium exchange between hydrogen and methylamine occurs, an equilibration between the ortho-para modifications is simultaneously catalyzed. Thus, equilibrium rather than normal mixtures of these modifications shall be considered, but the differences are small and appear only at the low end of the temperature range.

In treating isotopic exchange one is generally interested in the total atom fraction of isotopes over all isotopic molecules of a substance, rather than molar fractions of individual species. Isotopic equilibria are therefore specified over the full range of atom fractions of any isotope in either of the involved substances. The manipulation used here for the estimation of the separation factor as a function of the atom fraction x of deuterium in the methylamine is outlined below.

For any two substances 1 and 2 containing p and q hydrogen atoms, the molar fractions of isotopic species containing j deuterium atoms are denoted as x_j and y_j, respectively. The ratios of the molar fractions are given by

$$u_j = x_j/x_{j-1} \qquad v_j = y_j/y_{j-1}$$

The following equations are identical for both substances, provided the designations are replaced accordingly. The atom fraction x of deuterium over all isotopic species can be represented as follows:

$$x = \frac{1}{p}\sum_{j=1}^{p} jx_j = \frac{\sum_{i=1}^{p}\prod_{j=1}^{i} u_j}{p\sum_{i=0}^{p}\prod_{j=1}^{i} u_j} \tag{27}$$

Introduction of the internal equilibrium constant K_j defined by the ratios of the partition functions Q_j gives

$$K_j = \frac{Q_j^2}{Q_{j-1}Q_{j+1}} = \frac{u_j}{u_{j+1}} \tag{28}$$

All values of u_j in eq 27 can now be replaced by a single value, e.g., by u_j from eq 25, whereby

$$x = \frac{1}{p}\,\frac{\sum_{i=1}^{p} iu_1^{\,i}\prod_{j=1}^{i-1} K_j^{\,j-i}}{\sum_{i=0}^{p} u_1^{\,i}\prod_{j=1}^{i-1} K_j^{\,j-i}} \tag{29}$$

For a given value of x ($0 < x < 1$) the value of u_1 can be found by solving the following equation of order p

$$\sum_{i=0}^{\mathrm{p}} u_1^{\,i}(px - i)\sum_{j=1}^{i-1} K_j^{\,j-i} = 0 \tag{30}$$

Once u_1 is known, any value of v_j, e.g., v_1, can be found by using the external equilibrium constant

$$K_{1\mathrm{e}} = \frac{(Q_1/Q_0)_1}{(Q_1/Q_0)_2} \tag{31}$$

where the index outside the brackets designates the substance for which the ratio Q_1/Q_0 of the partition functions is taken. The value of v_1 is

$$v_1 = u_1/K_{1\mathrm{e}} \tag{32}$$

The value of y is now equal to the right-hand side of eq 29 in which p is replaced by q, u_1 by v_1, and all values K_j shall be taken for the substance 2. Finally, for each value

TABLE X: Deuterium Separation Factor between Gaseous Methylamine and Hydrogen

temp, K	atom fraction of deuterium in methylamine: 0	0.2	0.4	0.6	0.8	1.0
	deuterium separation factor					
150	24.5	24.8	25.0	25.1	24.5	17.4
175	14.4	14.5	14.6	14.4	13.9	10.6
200	9.67	9.69	9.66	9.53	9.12	7.37
225	7.08	7.07	7.02	6.89	6.57	5.55
250	5.52	5.49	5.44	5.32	5.08	4.44
275	4.50	4.48	4.42	4.32	4.13	3.70
300	3.81	3.78	3.73	3.64	3.49	3.19
350	2.94	2.91	2.86	2.80	2.70	2.53
400	2.42	2.40	2.36	2.32	2.25	2.14

TABLE XI: Deuterium Separation Factor between Liquid Methylamine and Its Vapor

temp, K	atom fraction of deuterium in the liquid: 0	0.2	0.4	0.6	0.8	1.0
	deuterium separation factor					
180	1.100	1.101	1.102	1.102	1.101	1.100
200	1.073	1.074	1.074	1.074	1.074	1.073
225	1.051	1.051	1.051	1.051	1.051	1.051
250	1.036	1.036	1.036	1.036	1.036	1.036
275	1.025	1.025	1.025	1.025	1.025	1.025
300	1.017	1.018	1.018	1.018	1.018	1.017
350	1.008	1.008	1.008	1.008	1.008	1.008
400	1.002	1.002	1.002	1.002	1.002	1.002
430	1.000	1.000	1.000	1.000	1.000	1.000

of x (and each temperature) the separation factor α is calculated by using the following equation:

$$\alpha = \frac{x/(1-x)}{y/(1-y)} \tag{33}$$

At the boundary limits the following formulas are derived by a limit analysis

$$\lim_{x\to 0} \alpha = \frac{q}{p} K_{1e} \tag{34}$$

$$\lim_{x\to 1} \alpha = \frac{p}{q} \frac{\prod_{j=1}^{q-1} K_{j2}}{\prod_{j-1}^{p-1} K_{j1}} K_{1e} \tag{35}$$

where the second index of K_j designates the substance.

The above method of calculation has been used for the evaluation of the equilibria between gaseous methylamine and hydrogen, as well as between liquid methylamine and its vapor, which are considered as substances 1 and 2, respectively. In the second case, K_{1e} is equal to the previously mentioned function α_v, $K_{j1} = K_{j2}$ for all values of j, and $p = q = 2$. The results of the calculations are summarized in Tables X and XI. It can be seen that the deuterium separation factor between the gaseous methylamine and hydrogen depends quite strongly on the deuterium level, expressed as the atom fraction x in methylamine. It follows from eq 34 and 35 that $\alpha(0) = \alpha(1) = \alpha_v$; however, the value of α_v between $x = 0$ and $x = 1$ is slightly higher, passing over a maximum.

Acknowledgment. We thank F. W. R. Molson (CRNL) for improving the Schiff base technique and J. G. Wesanko (CRNL) for fabricating the exchange cell.

Appendix

Treatment of Inversion and Internal Rotation Modes. (i) *NH_2 Inversion (Wagging Mode).* The kinetic coefficient $g^{44}(\tau)$ and the kinetic determinant $g = g_1(\tau)g_2(\tau)$ are given explicitly by

$$g^{44}(\tau) = (g_{11,0} + g_{11,1} \cos \tau)/g_1(\tau)$$

$$g_1(\tau) = g_{1,0} + g_{1,2} \cos 2\tau$$

$$g_2(\tau) = g_{2,0} + g_{2,1} \cos \tau + g_{2,2} \cos 2\tau$$

and may directly be calculated from structural parameters via the equations

$$g_{1,0} = (\Theta + \tfrac{1}{2}I_{55})I_{44} - \tfrac{1}{8}\bar{\Theta}^2$$

$$g_{1,2} = -\tfrac{1}{8}\bar{\Theta}^2$$

$$g_{2,0} = \{[\Theta + \tfrac{1}{2}I_{44} + \bar{I}_{44} + \tfrac{1}{2}I_{55}][\tfrac{1}{2} + \bar{I}_{44}] - \tfrac{1}{2}I_{44}^2 - \tfrac{1}{8}\bar{\Theta}^2\}I_{55}$$

$$g_{2,1} = -\bar{\Theta}I_{44}I_{55}$$

$$g_{2,2} = [-\tfrac{1}{2}I_{44}(\Theta + \tfrac{1}{2}I_{55}) + \tfrac{1}{8}\bar{\Theta}^2]I_{55}$$

$$g_{11,0} = \Theta + I_{44} + \tfrac{1}{2}I_{55}$$

$$g_{11,1} = \bar{\Theta}$$

$$\Theta = m_N X_{30}^2 + m_C(R_{30} + X_{30})^2 + 2m_{H1} X_{30}^2 + 3m_{H2}(-R_{30} - X_{30} + R_{20} \cos \Theta_0)^2$$

$$\bar{\Theta} = 4m_{H1}R_{10}X_{30} \cos \delta_0$$

$$I_{44} = 2m_{H1}(1 - (2m_{H1}/M))R_{10}^2 \cos^2 \delta_0$$

$$\bar{I}_{44} = 2m_{H1}R_{10}^2 \sin^2 \delta_0$$

$$I_{55} = 3m_{H2}R_{20}^2 \sin^2 \theta_0$$

$$X_{30} = -(m_C/M)R_{30} + 3(m_{H2}/M)(-R_{30} + R_{20} \cos \theta_0)$$

where m_{H1} and m_{H2} stand for the mass of hydrogen in the amino and methyl groups and M is the total mass of methylamine, and the structural parameters are defined in Table III. For determination of the energy levels by rotation–inversion theory a potential function of the form[34,35]

$$V(\tau) = y(\tau) - y(\tau_e)$$

$$y(\tau) = a \cos \tau + b/(1 + c \cos \tau)$$

was chosen, where τ_e stands for the inversion angle of the local minimum of the inversion potential. The constants a, b, and c were determined from the observed fundamental transitions of the amino wagging mode and some inversion splittings of the isotopic species $CH_3{}^{14}NH_2$, $CH_3{}^{14}ND_2$, $CH_3{}^{15}NH_2$, $CD_3{}^{14}NH_2$.[25,36] When the rotation–inversion program was used, the inversion levels up to 3000 cm^{-1} were calculated and used for evaluation of Q_{inv}. No details of the calculation are reproduced here.

(ii) *CH_3 Internal Rotation.* Energy levels and eigenfunctions of the methyl group internal rotation problem were defined by eq 19 and 2 where (cf. (i))

$$g^{55}(\tau) = \{(\Theta + \tfrac{1}{2}I_{44} + \bar{I}_{44} + \tfrac{1}{2}I_{55}) \times (\tfrac{1}{2}I_{44} + \bar{I}_{44} + I_{55}) - \tfrac{1}{2}I_{44}^2 - \tfrac{1}{8}I_{55}^2 - \bar{\Theta}(I_{44} + I_{55}) \cos \tau + [\tfrac{1}{2}I_{44}(-\Theta + \tfrac{1}{2}I_{55}) + \tfrac{1}{8}\bar{\Theta}^2] \cos 2\tau\}/g_2(\tau)$$

$$g_2(\tau) = (\Theta + \tfrac{1}{2}I_{44} + \bar{I}_{44} + \tfrac{1}{2}I_{55})(\tfrac{1}{2}I_{44} + \bar{I}_{44}) - \tfrac{1}{2}I_{44}^2 - \tfrac{1}{8}\bar{\Theta}^2 - \bar{\Theta}I_{44} \cos \tau[-\tfrac{1}{2}I_{44}(\Theta + \tfrac{1}{2}I_{55}) + \tfrac{1}{8}\bar{\Theta}^2]\cos 2\tau$$

$$I_{55} = 3m_{H2}R_{20}^2 \sin 2\delta_0$$

As mentioned already in section 3.1, solution of the internal rotation problem has been sought by approximating the Hamiltonian H^{inro} by setting g^{55} equal to $\langle g^{55}(\tau)\rangle$ where

$$\langle g^{55}(\tau)\rangle = (\psi^{inv}_{\Gamma_1,1}, g^{55}(\tau)\psi^{inv}_{\Gamma_1,1})$$

The latter quantity is directly available from the structural parameters through the foregoing formula and the ground

J. Phys. Chem. 1980, 84, 2179–2185 2179

state energy eigenfunction of the inversion problem. Numerical solution of the approximate energy eigenvalue problem again has been made by infinite matrix diagonalization. For illustration we give below the lowest torsional energy levels for CH_3NH_2 based on barrier values reported by Itoh[37,38] and Lide;[39] for this work $V_3 = 691.1$ cm^{-1} has been chosen.

$\Gamma(0+)(g{=}1)$: 144, 600, 926, 1577, 2519
$\Gamma(0-)(g{=}1)$: 414, 910, 1577, 2519
$\Gamma(1)(g{=}2)$: 144, 408, 637, 773, 1105, 1325, 1860, 2174

Supplementary Material Available: The complete Table II containing the 66 experimental points displayed in Figure 2 (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) K. Bar-Eli and F. S. Klein, *J. Chem. Soc.*, 3083 (1962).
(2) A. R. Bancroft and H. K. Rae, Proceedings of Symposium on the Technical and Economic Aspects of Heavy Water Production, Turin, Italy, 1970, p 47, AECL-3684.
(3) M. Perlman, J. Bigeleisen, and N. Elliott, *J. Chem. Phys.*, **21**, 70 (1953).
(4) J. Ravoire, P. Grandcollot, and G. Dirian, *J. Chim. Phys. Phys.-Chim Biol.*, **60**, 130 (1963).
(5) J. Bron and M. Wolfsberg, *J. Chem. Phys.*, **57**, 2862 (1972).
(6) I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water, Nuclear Energy Series," Div. III-4A, McGraw-Hill, New York, 1951, p 65.
(7) L. Silberring, to be submitted for publication.
(8) J. H. Rolston, J. den Hartog, and J. P. Butler, *J. Phys. Chem.*, **80**, 1064 (1976).
(9) R. D. Bardo and M. Wolfsberg, *J. Phys. Chem.*, **80**, 1068 (1976).
(10) J. D. Halliday and P. E. Bindner, *Can. J. Chem.*, **54**, 3775 (1976).
(11) J. P. Butler, J. H. Rolston, and W. H. Stevens, *ACS Symp. Ser.*, **No. 68**, 93 (1978).
(12) L. J. Jolley, *J. Chem. Soc.*, 1957 (1934).
(13) W. H. Stevens and W. Thurston, "The Determination of the D_2O Content of Heavy Water by Infrared Spectrophotometry", AECL Report, AECL-295, 1954.
(14) W. H. Stevens, J. G. Bayly, W. Thurston, and V. B. Kartha, "Heavy Water Analysis in the 1% to 99% D_2O Range by Infrared Spectrophotometry", AECL Report AECL-1391, 1961.
(15) D. M. Himmelblau, "Process Analysis by Statistical Methods", Wiley, New York, 1970, p 114.
(16) H. Wolff and A. Höpfner, *Z. Elektrochem.*, **66**, 149 (1962).
(17) H. Wolff, A. Höpfner, and H. M. Höpfner, *Ber. Bunsenges. Phys. Chem.*, **68**, 410 (1964).
(18) H. Wolff and A. Höpfner, *Ber. Bunsenges. Phys. Chem.*, **69**, 710 (1965).
(19) H. Wolff and A. Höpfner, *Ber. Bunsenges. Phys. Chem.*, **71**, 461 (1967).
(20) H. Wolff and R. Würtz, *Z. Phys. Chem. (Frankfurt am Main)*, **67**, 115 (1969).
(21) J. Bigeleisen, *J. Chem. Phys.*, **23**, 2264 (1955).
(22) G. N. Lewis and R. E. Cornish, *J. Am. Chem. Soc.*, **55**, 2616 (1933).
(23) J. Papezin, G. Jakli, G. Jancos, and W. A. Van Hook, *J. Phys. Chem.*, **76**, 743 (1972).
(24) A. Bauder, R. Meyer, and Hs. H. Günthard, *Mol. Phys.*, **28**, 1305 (1974).
(25) M. Tsuboi, A. Y. Hirakawa, T. Ino, T. Sasaki, and K. Tamagake, *J. Chem. Phys.*, **41**, 2721 (1964).
(26) T. K. Ha, private communication.
(27) A. Attanasio, A. Bauder, Hs. H. Günthard, and H. J. Keller, *Mol. Phys.*, **21**, 35 (1971).
(28) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959).
(29) T. Shimanouchi, Tables of Molecular Vibrational Frequencies, Part 2, *Natl. Stand. Ref. Data Ser.*, (*U.S., Natl. Bur. Stand.*), **No. 11** (1967); A. P. Gray and R. C. Lord, *J. Chem. Phys.*, **26**, 690 (1957).
(30) H. Wolff and H. Ludwig, *J. Chem. Phys.*, **56**, 5278 (1972).
(31) G. Dellepiane and G. Zerbi, *J. Chem. Phys.*, **48**, 3573 (1968).
(32) H. W. Woolley, R. B. Scott, and F. G. Brickwedde, *J. Res. Natl. Bur. Stand.* (*U.S.*), **41**, 379 (1948) (Research Paper RP 1932).
(33) R. Kosloff, R. D. Levine, and R. B. Bernstein, *Mol. Phys.*, **27**, 981 (1974).
(34) A. Attanasio, A. Bauder, Hs. H. Günthard, and H. J. Keller, *Mol. Phys.*, **21**, 35 (1971).
(35) A. Attanasio, Thesis No. 5035, ETH Zurich, 1973.
(36) M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, *J. Mol. Spectrosc.*, **22**, 272 (1967).
(37) T. Itoh, *J. Phys. Soc. Jpn.*, **11**, 264 (1956).
(38) K. Shimoda, T. Nishikawa, and T. Itoh, *Phys. Rev.*, **98**, 1160 (1955).
(39) D. R. Lide, *J. Chem. Phys.*, **27**, 343 (1957).
(40) K. Takagi and T. Kojima, *J. Phys. Soc. Jpn.*, **30**, 1145 (1971).
(41) H. C. Urey and D. Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933).
(42) G. Herzberg and A. Monfils, *J. Mol. Spectrosc.*, **5**, 482 (1960).
(43) L. Wolniewicz, *J. Chem. Phys.*, **45**, 515 (1966).
(44) R. B. Bernstein, private communication, 1978.

Ion Distributions in Lamellar Liquid Crystals. A Comparison between Results from Monte Carlo Simulations and Solutions of the Poisson–Boltzmann Equation

Bo Jönsson,[†] **Håkan Wennerström,***[†] **and Bertil Halle**[‡]

Divisions of Physical Chemistry, Chemical Center, S-220 07 Lund 7, Sweden

(Received: December 18, 1979)

Monte Carlo (MC) simulations have been performed for an ionic system between two parallel uniformly charged plates modeling the conditions found in lamellar lyotropic liquid crystals. The results are used to assess the accuracy of the statistical-mechanical approximations leading to the Poisson–Boltzmann (PB) equation. In general there is a good agreement between the MC simulations and the results obtained from the PB equation. This applies to the ion distribution and to a lesser extent to the energy. In particular the PB equation predicts the correct asymptotic behavior as the distance between the plates is increased. In the MC simulations there is a slight increase in the ion concentration close to the walls compared to the PB solution. This is due to the fact that in the MC simulations one allows for correlations between the ions, whereas the PB equation is derived under the assumption that the pair correlation function is constant. It is shown that the accumulation of ions close to the walls is solely due to the repulsions between the ions, and it is argued that ion binding in a polyelectrolyte system can be understood as caused by the incapability of the bulk solution to sustain a substantial net charge over moderately large distances.

Introduction

The physical–chemical properties of charged macromolecules and aggregates in an aqueous medium are strongly influenced by electrostatic effects. A large species having a high surface charge will attract counterions to reduce the electrostatic repulsions at the surface. When studying the ion binding in such systems, one either can be directly interested in the ion distribution as it is probed in a spectroscopic[1–4] or kinetic[3,5] experiment or can focus

---

[‡] Division of Physical Chemistry 1.

[†] Division of Physical Chemistry 2.

0022-3654/80/2084-2179$01.00/0