stituted quinolines. This observation is interesting in that a quantitative correlation between the forces responsible for the alteration of water structure can be found out using these hydrochlorides. It should be realized that nitrogen positive centres and their stabilization by various factors are of primary importance in water structure alterations[3]. The hydroxy group in 8-hydroxyquinoline hydrochloride may reduce the charge density on nitrogen compared to quinoline hydrochloride and thereby reduce the structure-breaking ability of the nitrogen positive centre so much so that it eventually becomes structure-making. The marginal structure-breaking effect of quinoline hydrochloride should be noted (a difference of 1·7 ppm only, Table 1). The above fact is supported from the experiment with 8-nitro-quinoline hydrochloride wherein an enhanced structure-breaking effect is observed due to the resonance stabilized increase in charge density on nitrogen by the electron withdrawing nitro group. Apart from this electronic effect a steric effect is indicated from the enhanced structure-making effect of the hydrochloride of 2-methylquinoline. Similar structure-making effect has been reported[3] for 2,6-dimethylpyridinium chloride and bromide.

The experiment with N,N-dimethyl-p-toluidine hydrochloride is interesting as it is not altering the structure of water. It contains sp^3-hybridized nitrogen and thus does not become structure-making in spite of it having three methyl groups.

Hydration of ions in aqueous solutions is generally characterized by the hydration number. However, there is always a possibility of exchange between the closest molecules of water in an aqueous solution and hence the residence time of ionic hydration has been described[2] to be more appropriate for characterizing hydration of ions. Residence time depends on the quantity ΔE_i which is the difference between the energy required by a water molecule to escape from the immediate neighbourhood of the ion and the energy in free water of aqueous solution required for a water molecule to replace its neighbour. In cases for which $\Delta E_i > 0$, termed positive hydration, exhange of nearest water molecules is not frequent. Cases for which $\Delta E_i < 0$ are termed negative hydration. Positive hydration alone is not enough to cause a given ion to move with its hydration shell. Strong hydration with large positive ΔE_i is necessary for such a movement. Extreme cases for such structure-making ions can be said to be present in crystalline hydrates containing coordinated water molecules. While removing this coordinated water by distillation, heavy water comes out first due to the reasons described earlier[1]. The deuterium content of the first two fractions of water removed from 500 g of crystalline $Fe(NO_3)_3.9H_2O$ has been found to be 232·6 and 213·0 ppm respectively. Selective excitation with infrared light of wave-number 1455 cm^{-1}, for example, would reduce the nucleophilicity of HDO molecule further and facilitate its removal.

It can be concluded that in the cases of strong hydration (large positive ΔE_i) where the entire hydration complexes are altered and in extreme cases of solutions of structure-making salts such as

crystalline hydrates containing coordinated water, heavy water is removed easily compared to light water. This offers a new method for the enrichment and production of heavy water[1]. On the other hand, ions whose residence time of hydration is small and ΔE_i is negative, less of heavy water will come in the initial fractions when used in appropriate concentration. Here again it is the major role of the structure of water and its destruction by structure-breaking solutes that makes the development of negative hydration feasible which can be utilized to improve heavy water production by electrolysis and distillation. Urea has been found[1-5] to be a suitable structure-breaking species.

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Computation of Deuterium Isotope Effect in Metal Hexaammine-Ammonia Exchange Process

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Several metal hexaammine complex-ammonia exchange systems have been examined for equilibrium isotope effect and equilibrium constants, and separation factors have been calculated from the normal modes of vibrations. The results indicate suitability of $Ni(NH_3)_6^{2+}$-ammonia system for large-scale deuterium enrichment. The magnitude of the isotope effect is shown to be dependent on the harmonicity of the N-H bond vibrations.

THE ammonia exchange in some metal hexaamine complex-ammonia systems is very rapid[1] and is, therefore, a suitable reaction for the deuterium enrichment by exchange process provided the equilibrium constants are high enough for deuterium-protium separation to take place appreciably. To determine the extent of isotope separation, an investigation has been carried out to calculate deuterium isotope effect in such systems by the methods of Bigeleisen and Mayer[2] and Urey[3] using the best available data on the vibrational frequencies. The

results of the investigation are presented in this note and some of the factors influencing them are discussed.

Method of calculation — The exchange reaction between the metal hexaammine complex may be written as

$$M(NH_3)_6^{Z+} + 6ND_3 \rightleftharpoons M(ND_3)_6^{Z+} + 6NH_3 \qquad \ldots(1)$$

The equilibrium constant for the reaction is given by statistical thermodynamics as

$$K = \frac{(QD/QH) \text{ complex}}{(QD/QH) \text{ 6 ammonia}} \qquad \ldots(2)$$

and the separation factor (α) for ammonia-d_3 is given by Eq. (3)

$$\alpha = K^{1/6} \qquad \ldots(3)$$

The QD and QH are respectively the molar partition function for the deuterated species and the non-deuterated species. At ordinary temperatures when the translation and rotation of the molecules are adequately described by classical mechanics, and under Born-Oppenheimer approximation the reduced partition function ratios (RPFR) of Bigeleisen and Mayer[4] for two isotopic molecules, are given by Eq. (4)

$$RPFR = (S/S'f) = \prod_i^{3N-6} \frac{ui \ (1-e^{-ui'}) \ e^{-ui/2}}{ui' \ (1-e^{ui}) \ e^{-ui'/2}} \qquad \ldots(4)$$

where S and S' are the symmetry numbers of the two molecules and the summation is over all the $(3N-6)$ normal vibrations of the molecules and

$$u = hcv/kT \qquad \ldots(5)$$

where all the symbols have their usual meaning. The primed notations represent lighter isotope. In this case of symmetric substitution, the symmetry members S and S' are identical and the value of α is given by

$$\alpha = K^{1/6} = \frac{(RPFR) \ 1/6 \text{ complex}}{(RPFR) \text{ ammonia}} \qquad \ldots(6)$$

The calculation here is for perfect gases. However, the results are applicable without correction even to the condensed phases because isotope effects on vapour pressure are usually quite small as compared to isotope effect on chemical equilibrium constants so that non-bonding intermolecular interactions can be ignored[4].

In an octahedral metal hexaammine complex the $3N$-6 ($= 69$) normal frequencies are reduced to 63 as six of them, caused by rotation of the ligands around the M-N bond, are redundant. The remaining 63 frequencies are distributed in various symmetry species of the O_h group as follows: M-N stretching ($A1g$, Eg, $F1u$), N-M-N bending ($F1u$, $F2g$, $F2u$), symmetric N-H stretching ($A1g$, Eg, $F1u$), asymmetric N-H stretching ($F1g$, $F1u$, $F2g$, $F2u$), symmetric H-N-H deformation ($A1g$, Eg, $F1u$), degenerate H-N-H deformation ($F1g$, $F1u$, $F2g$, $F2u$), NH_3 rocking ($F1g$, $F1u$, $F2g$, $F2u$). Out of these $A1g$, Eg and $F2g$ are Raman active and $F1u$ is infrared active while $F1g$ and $F2u$ are inactive. The six normal vibrations of ammonia are distributed in two A and two E symmetry species.

For rigorous calculation of RPFRs and hence the equilibrium constants and separation factors, all the frequencies in each species should be completely known. However, the Raman data are available only for cobalt hexaammine complex and its deuterated analogue while inactive species $F1g$ and $F2u$ are not available. To find the isotope effect in such a case, only infrared frequencies of $F1u$ species have been used for Ni, Mg, Ir and Rh complexes assuming the vibrations of all the other species to be degenerate with that of $F1u$ species. The justification for this assumption is given elsewhere in this paper. Thus the infrared frequencies have following degeneracies: M-N stretching (6), N-M-N bending (9), symmetric N-H stretching (6), asymmetric N-H stretching (12), symmetric H-N-H deformation (6), degenerate H-N-H deformation (12) and NH_3 rocking (12). For the purpose of calculation, the ammonia and ammonia-d_3 frequencies have been taken from the values compiled by Shimanouchi[5]. The values of vibrational frequencies of cobalt complex are from Siebert and Eysel[6], those of magnesium complex are from Plus[7] and of the nickel complex the values are those computed by Jeevanadam and Gupta[8] using Wilson's FG method. The frequencies for platinum group metals are those given by Griffith[9]. The normal vibrations are slightly altered in the presence of different anions. For all the complexes the frequencies used here were obtained when chloride was the anion. A Fortran IV programme was written to solve Eqs. (4) and (6) and was run on a BESM-6 computer to obtain values of the separation factor at various temperatures.

The separation factors obtained are given in Table 1. The highest separation factor has been obtained for Ni and the lowest for Mg complexes. Log α tends towards zero at high temperatures. The separation factor for cobalt complex-ammonia system has been calculated first by considering all the available frequencies from infrared and Raman spectrum (method A) with $F1g$ and $F2u$ both degenerate with $F1u$ and then by considering infrared frequencies only (method B). The negligible difference between the values of the two quantities (0·13% at 25°) shows that the approximation of taking vibrations of all the symmetry species to be degenerate with infrared active one is quite good. The reason for this is that ligand vibrational

TABLE 1 — SEPARATION FACTORS AT VARIOUS TEMPERATURES FOR METAL HEXAAMMINE-AMMONIA SYSTEMS

Temp. °C	Co³⁺ Method A	Co³⁺ Method B	Ni²⁺	Rh³⁺	Ir³⁺	Mg²⁺
−50	2·098	2·105	2·637	1·789	1·680	1·410
−25	1·837	1·841	2·278	1·598	1·514	1·312
0	1·654	1·657	2·028	1·463	1·395	1·242
25	1·521	1·523	1·848	1·362	1·307	1·189
50	1·420	1·422	1·711	1·286	1·239	1·148
75	1·343	1·344	1·606	1·228	1·187	1·117
100	1·282	1·283	1·513	1·181	1·146	1·092
125	1·233	1·234	1·456	1·144	1·113	1·072
150	1·194	1·194	1·401	1·114	1·086	1·056
175	1·162	1·162	1·356	1·089	1·064	1·043
200	1·135	1·135	1·318	1·069	1·046	1·034

frequencies hardly change from one symmetry species to another. The M-N stretching and N-M-N bending frequencies do vary with symmetry species but the primary isotope effects are due to change in force constants of only the bonds involving isotopically substituted atom[4] and therefore these skeletal modes have little effect on the value of the separation factor.

The equilibrium isotope effect is a function of the vibrational frequencies of the isotopic molecules and the contribution by the factor $ui/u'i$ is dominant at ordinary temperatures[4,10]. This is evident from expressions (4) and (6). The ratio $ui/u'i$ also gives the harmonicity of the ith vibration with the value 1·414 for perfectly harmonic vibration and decreases with increasing anharmonicity. In particular case of ammines the primary isotope effect would result from the NH vibrations only. Thus the anharmonicity of these vibrations, when ammonia is coordinated to different cations, should be an indication of the magnitude of the isotope effects in different ammines, though a quantitative agreement should not be expected due to obvious reasons. From Table 2 we see that the ratio vH/vD (hereafter referred to as harmonicity) is in the order $Ni^{2+} > Co^{3+} > Rh^{3+} > Mg^{2+} > Ir^{3+}$ for symmetric stretching vibrations, whereas the separation factors are in the order $Ni^{2+} > Co^{3+} > Rh^{3+} > Ir^{3+} > Mg^{2+}$. The failure of above reasoning in the case of the last two complexes is due to neglect of all other NH vibrations except the symmetric stretching ones. The harmonicity of Ir complex is greater than that of Mg in the case of asymmetric stretching, degenerate bending and rocking vibrations while it is less in the case of symmetric stretching and symmetric bending. Since all the vibrations affect equally the calculation of the equilibrium constant, the isotope effect may not be strictly assigned due to only one of the many vibrations. However, from Table 2 it can be seen that the NH_3 rocking vibration shows trends exactly identical to the isotope effect. This treatment is particularly complex in that there are five different vibrations involving appreciable movement of isotopically substituted atoms; with lesser number of vibrations in smaller molecules the relationship between isotope effect and harmonicity of the vibrations in a series of similar compounds is expected to be more straightforward.

The high value of the separation factors obtained indicate suitability of these exchange reactions as a method for enriching deuterium on a large scale. For Co^{3+}, Rh^{3+} and Ir^{3+} hexaammine complexes, the rate of exchange of ammonia molecules (or lability) is small[1], requiring use of a catalyst. However, in the Ni^{2+} complex, for which the separation factor is also largest, the ammonia ligands are highly labile by themselves[1], with the rate constant.

$$k = \frac{\text{Reaction rate}}{6[Ni]} = 1·0 \times 10^5 \text{ sec}^{-1} \text{ at } 25° \text{ (ref. 13)}$$

TABLE 2 — HARMONICITY OF DIFFERENT VIBRATIONS IN RELATION TO ISOTOPE EFFECT

vH/vD	Ni^{2+}	Co^{3+}	Rh^{3+}	Ir^{3+}	Mg^{2+}
NH sym. stretch	1·401	1·394	1·376	1·353	1·372
NH_3 rock	1·324	1·315	1·299	1·295	1·289

Therefore this reaction is much more suitable than the rest for the above purpose.

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Application of Henderson's Partition Function in the Computation of Sound Velocity & Solubility Parameter

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Sound velocity in liquid hydrogen and solubility parameters of liquid solvents such as CS_2, ether, C_6H_6, CH_3Cl, Br_2, N_2O, C_2H_6, dimethyl ether, CO, He, Cl_2, O_2, N_2, A and H_2 have been calculated using Henderson's partition function. Calculated values are in agreement with the observed values.

IN our previous work[1-3], it was shown that the significant liquid structure theory as developed by Henderson[4] for rigid sphere molecules could reproduce the properties of real fluids in a good measure. It is, however, important for a theory of this type, which is based on an intuitive division of the partition function into gas-like and solid-like degrees of freedom, to be of general nature and valid for diverse kind of properties. With this end in view, we report our computation of sound velocity in liquids and solubility parameters of various liquid solvents.

Sound velocity — It has been established[5] that sound velocity (C_0) in a medium is given by the relation (1)

$$C_0 = \left[\frac{\gamma}{\beta_T \rho}\right]^{\frac{1}{2}} = \left[\frac{C_p}{C_v \beta_T \rho}\right]^{\frac{1}{2}} \quad \ldots(1)$$

where γ is C_p/C_v, β_T is isothermal compressibility, ρ is density of liquid and C_p and C_v are heat capacities at constant pressure and volume respectively. Again, C_p is related with C_v by relation (2)

$$C_p = C_v + \frac{\alpha^2 VT}{\beta_T} = C_v + \frac{\alpha^2 MT}{\beta_T \rho} \quad \ldots(2)$$