The data given in Table 4 indicate that our calculated results by the simplification method are comparable to those given by Brand et al.⁹ using Frank-Condon principle. On the other hand, the results obtained after applying the Jacobi's refined method are nearly the same as those given by Lombardi¹⁰ using the analysis of rotational structure. He based his calculations assuming the change in the C=S bond to be equal to that given by Brand. This may be the reason for his results not coinciding with our results.

The authors wish to express their gratitude to Prof. M. I. Nasser, National Research Centre, Cairo, Egypt for his valuable discussion and suggestions.

References

Equilibrium Deuterium Isotope Effects in Formic Acid-Hydrogen Exchange

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Received 16 July 1979; accepted 23 August 1979

Deuterium separation factors for formic acid-hydrogen exchange have been calculated as function of temperature and deuterium concentration in hydrogen, using the spectroscopic data. From the temperature dependence of the separation factors, the enthalpy of isotopic exchange reaction has been calculated.

O

ONE of the most important parameters in determining the feasibility of a particular process for large scale enrichment of deuterium is the separation factor. Before determining the separation factor for a particular exchange reaction experimentally, it is desirable that an idea be had of the value of this factor.

In what follows an attempt is made to calculate the separation factors for the formic acid-hydrogen exchange over a wide range of temperatures and of deuterium concentrations in hydrogen.

The deuterium separation factor, \( a \), between formic acid and hydrogen in a gaseous mixture containing
all the isotopic species of these molecules at equilibrium, is given by Eq. (1).

\[
\alpha = \frac{y}{1-y} \times \frac{1}{x/(1-x)} \quad \ldots (1)
\]

where \(x\) and \(y\) are, respectively, the D atom fractions among hydrogen atoms in formic acid and hydrogen and are given by Eqs (2) and (3) respectively.

\[
x = \frac{\text{HCOOD}}{\text{HCOOH} + \text{HCOOD}} \quad \ldots (2)
\]

\[
y = \frac{\text{D} + \text{D}_2}{\text{H}_2 + \text{D} + \text{D}_2} \quad \ldots (3)
\]

In Eqs (2) and (3) quantities within parenthesis refer to the mole fractions in the mixture.

The separation factors between gaseous formic acid and gaseous hydrogen can be computed from the knowledge of exchange equilibria involving different isotopic counterparts of formic acid and hydrogen molecules. For calculating overall deuterium separation factors for formic acid and hydrogen exchange, the exchange reactions (4) and (5) should be considered.

\[
\text{HCOOH} + \text{HD} \rightleftharpoons \text{HCOOD} + \text{H}_2 \quad \ldots (4)
\]

\[
\text{H}_2 + \text{D}_2 \rightleftharpoons 2 \text{HD} \quad \ldots (5)
\]

Let \(K_1\) and \(K_2\) represent the equilibrium constants for the reactions (4) and (5) respectively, by suitable algebraic substitutions, it can be shown that,

\[
\alpha = \frac{K_1K_2(2 + A)}{K_2 + 2A} \quad \ldots (6)
\]

where

\[
A = \frac{(\text{HD})}{(\text{D}_2)} = \frac{p}{(1-2y)} \quad \ldots (7)
\]

Thus in the above expressions, in order to calculate the separation factors, we should have precise knowledge of the equilibrium constants \(K_1\), and \(K_2\) and \(y\), the deuterium fraction in hydrogen molecules.

Bigeleisen and Meyer\(^1\) have shown that the equilibrium constant for any isotopic exchange reaction can be calculated from the reduced partition function ratios for the corresponding isotopic pairs taking part in the exchange reaction. This procedure has been described by Dave and coworkers\(^5\) for ammonia-hydrogen exchange.

For any isotopic exchange reaction, say Eq. (4) the corresponding equilibrium constant \(K_1\) is given by

\[
K_1 = \frac{[\text{HCOOD}][\text{HCOOH}]}{[\text{HD}][\text{H}_2]} \quad \ldots (8)
\]

\[
K_1 = \left(\frac{s_{\text{HCOOH}}/s_{\text{HCOOD}}}{s_{\text{HD}}/s_{\text{D}}}\right) \left\{\frac{s/s'}{f'(\text{HCOOD})} \frac{s/s'}{f'(\text{HCOOH})}\right\} \quad \ldots (9)
\]

where \(s_{\text{HCOOH}}, s_{\text{HCOOD}}, s_{\text{HD}}\) and \(s_{\text{D}}\) are the symmetry numbers of the isotopic species \(\text{HCOOH}, \text{HCOOD}, \text{H}_2\) and \(\text{HD}\) respectively and (\(s/s'\)'s) are the reduced partition function ratios.

For the present study we have considered that except for the contribution due to vibration, all other contributions due to translational, electronic, nuclear spin, etc. tend to cancel out\(^6\) and correspondingly

\[
\left\{\frac{s/s'}{f'(\text{HCOOD})} \frac{s/s'}{f'(\text{HCOOH})}\right\} \quad \ldots (10)
\]

where \(V\)'s represent the vibrational partition functions. The corresponding contribution due to rotational partition functions, generally comes out less than \(1\%\) and hence it has been neglected.

For the exact evaluation of zero point energy of the molecule, the effect of anharmonicity of the molecular vibrations should be taken into consideration. Unfortunately no information regarding the

\[
\text{Temp. } ^\circ\text{K} \quad K_1 \quad K_2
\]

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\[
\text{F}i\text{g. 1 - Plot of ln } \alpha \text{ versus } 1/T \text{ for formic acid-hydrogen exchange.}
\]
Table 2 — Overall Deuterium Separation Factors for HCOOH-H$_2$ Exchange

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The separation factors decrease with increase in temperature. The plot of ln $\alpha$ against $1/T$ is linear and data fit the Eq. (11)

$$\ln \alpha = \frac{A}{T} + B \quad \ldots(11)$$

where $A$ corresponds to the heat of isotopic exchange reaction between formic acid and hydrogen and is found to be 4.26 kJ mole$^{-1}$. This temperature dependence corresponds to low deuterium concentrations (less than $1 \times 10^{-3}$).

The concentration dependence of the separation factors follows usual pattern as can be seen from Table 2. The separation factors decrease with increasing deuterium content of the system.

Depending on the catalysts used, formic acid is capable of undergoing decomposition as HCOOH $\rightarrow$ H$_2$ + CO$_2$. This reaction can provide the reflux mechanism and hence this process can be easily adopted for monothermal operation.

The separation factors are also reasonably high and vapour pressures are lower and if suitable catalysts can be developed to give faster exchange rates, this process could provide an alternative route to large scale separation of deuterium.

We are very thankful to Shri S. Fareeduddin and Shri P. G. Deshpande for their interest and encouragement, to Shri D. N. Bhatnagar for suggestions and discussions and to Mrs. Divekar for her help in calculations and computer programming.

References


Decay of Dissolution Potential of Some Electrolytes

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The decay of dissolution potential has been studied for seven electrolytes containing zero to six molecules of water of crystallization. It is found that the number of water molecules of crystallization influences the nature of the decay curves.

Our previous work has shown that the nature of decay of dissolution potential is somewhat influenced by the number of water molecules of crystallization associated with the electrolytes. The purpose of the present note is to study the decay of dissolution potential of a series of electrolytes containing zero to six water molecules of crystallization.

The electrolyte was deposited on a platinum electrode by the process of controlled crystallization from a solution of the electrolyte saturated at 70°C and then dipped mechanically in the experimental cell filled with deionized water. The potential so developed was measured with the help of a VTVM (Philips GM 6001/90) by reference to the potential of another