

Equilibrium Constant for Protium-Deuterium Exchange Between Methanol and Water

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Summary The equilibrium constant for protium-deuterium exchange between methanol and water at 25 °C has been calculated from new measurements, employing vapour-phase exchange over supported platinum catalysts, of the deuterium separation factor between molecular hydrogen and liquid methanol.

CONSIDERABLE controversy surrounds the equilibrium distribution of trace quantities of deuterium between the hydroxy-group of methanol and liquid water.¹⁻³ Based on a random distribution of isotopes the application of statistics leads to a liquid phase equilibrium constant $K_1(l) = 0.500$ for equation (1). Recently Fenby⁴ has

$$\text{CH}_3\text{OH}(l) + \text{HDO}(l) \rightleftharpoons \text{CH}_3\text{OD}(l) + \text{H}_2\text{O}(l) \quad (1)$$

estimated $K_1(l) = 0.454$ from modified reduced partition function ratios at 25 °C and has compared these with experimental values which range from 0.45 to 0.6. An independent estimate of $K_1(l)$ can be made from a knowledge of the deuterium isotope separation factor between

molecular hydrogen and liquid water, $\alpha(\text{H}_2\text{O})$, together with the corresponding separation factor, $\alpha(\text{MeOH})$, for liquid methanol. We have recently measured $\alpha(\text{MeOH})$ at 25 °C and the weighted mean of 8 observations was 4.245 ± 0.008 (1 ± 0.25), where the indicated uncertainty represents the standard error of the mean.⁵

The technique and apparatus employed was similar to that used to determine the fractionation factor $\alpha(\text{H}_2\text{O})$ between liquid water and molecular hydrogen⁶ except that a platinum catalyst was suspended in the vapour space above the gently stirred liquid in the equilibration cell. With this procedure no liquid is in contact with the catalyst and exchange proceeds by equilibration of hydrogen with vapour in equilibrium with the liquid. The deuterium concentration of the liquid initially charged to the cell was calculated from the weights and deuterium concentrations of commercial samples of the liquid alcohols. Independent standards were prepared by the addition of weighed quantities of D_2O (99.74 wt%) to methanol. The calculated value agreed to within 1% of that measured for the liquid using both i.r. and n.m.r. spectroscopy.

The vapour phase exchange method appears to be of general utility and it eliminates the uncertainties arising when separation of chemical species is attempted prior to analysing the deuterium content of the liquid at equilibrium. The higher diffusion coefficients of the molecular species in the vapour phase, relative to those in the liquid phase, also significantly reduce the time required to establish equilibrium compared with the case when catalysts are present in the liquid phase.⁷ Once isotopic equilibrium was established, (*ca.* 30 min) no further exchange was observed over several days. This indicates that transfer of deuterium into the methyl group is negligible under these conditions.

The equilibrium constant $K_1(l)$ can be calculated from the expression $K_1(l) = \alpha(\text{MeOH})/2 \times \alpha(\text{H}_2\text{O}) = 4.245/2.381 = 0.56 \pm 0.02$. A corresponding value for exchange between the vapours, $K_1(g)$, was calculated from $K_1(l)$ and the vapour-liquid fractionation factors for methanol,⁸ $\alpha_v(\text{MeOH})$ and water⁶ $\alpha_v(\text{H}_2\text{O})$ where $K_1(g) = K_1(l) \times \alpha_v(\text{H}_2\text{O})/\alpha_v(\text{MeOH}) = 0.562 \times 1.079/1.05 = 0.58 \pm 0.02$. The errors indicated represent a 1% probable error in each determination of the separation factors involved. These results indicate that deuterium prefers to reside in the hydroxy-group of the alcohol rather than in that of water.

This result is contrary to that expected from Fenby's theoretical estimate derived from his modified reduced partition function ratios, calculated by summing over the vibrational frequencies of the isotopically substituted species and incorporating published vapour pressure isotope effects. He claimed good agreement with two early estimates of 0.50 (25 °C)⁹ and 0.481 \pm 0.015 (80 °C)¹⁰ as well

as with the average value of 0.46 \pm 0.02 reported by Kwart, Kuhn, and Bannister.² This agreement may be fortuitous in that comparison of his modified reduced partition function for HDO-H₂O at 25 °C (26.975) with that derived from the molecular potential functions¹¹ (24.573) indicates the approximate method has over-estimated the ratio by 9.8%. No corresponding comparison can yet be made for methanol. The use of molecular potential functions has been discussed elsewhere^{11,12} and they have recently been used to test the importance of the Born-Oppenheimer approximation in evaluating the fractionation effect between molecular hydrogen and water vapour.¹³

Further examination of the data of Kwart *et al.* shows that while they report a considerable range in the sensitivity of the spectrometer over the absorption intensities used, they have not applied any statistical averaging to take into account the wide range of precision (factor of 92) associated with their measurements. The most precise value of the equilibrium constant is given as $K_1(l) = 0.53 \pm 0.004$. A weighed mean of all data using weights proportional to the inverse square of the probable errors gives $K_1(l) = 0.526 \pm 0.012$ (1 ± 0.35) for the four observations. This estimate is more in line with the value reported here and can be compared with the 'best' estimates of $K_1(l) = 0.6$ in methanol and 0.6-0.7 in water, available from thermochemical data.³ Together these studies suggest that a more detailed theoretical evaluation of $K_1(l)$ is required.

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