ISOTOPIC SHIFT OF WATER BY DISTILLATION

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The isotopic shift of water by distillation has been observed by several authors⑴ mainly at the normal boiling temperature and pressure. We have determined the shift in a heavy water sample of 2.60% deuterium content on slow vacuum distillation at several lower temperatures.

Ten milligrams water was distilled each time from 20 g. of the same sample, which was kept at a constant temperature within a few hundredths of a degree. The distillation took place within 40 to 60 minutes at a temperature difference of about half a degree. The distillate was analysed by means of a micropycnometer⑵ and was compared with the original water sample as shown in the table.

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(1) Lewis and Cornish, *J. Am. Chem. Soc.*, **55** (1933), 2661. Hall and Jones, *ibid.*, **56** (1934), 749. Harada and Titani, *this Bulletin*, **10** (1935), 39.

(2) Gilfillan and Polanyi, *Z. physik. Chem.*, [A], **166** (1933), 254. The original method was improved by the authors and accuracy appreciably increased.

Deuterium Content of Distillates from 2.60% Heavy Water.

Temp. of distillation (°C.)	0.05	20.42	−5.94	−6.42	0.08	21.48	21.00
Deuterium content (%)	2.42	2.49	2.39	2.38	2.38	2.46	2.47

The deuterium content of the original water sample was measured from time to time during the experiment and was proved to be constant within limits of error.

The heterogeneous equilibrium studied here might be expressed by the following formula:

$$H_2O_{vap}+HDO_{liq}\text{-}xH_2O_{liq} = HDO_{vap}+H_2O_{liq}\text{-}xH_2O_{liq} ,$$

where xH_2O_{liq} denotes environments of the molecule in the liquid state. $H_2O_{liq}\text{-}xH_2O_{liq}$ may be a polymer. D_2O concentration was neglected here and environments both of H_2O and of HDO molecules were assumed to be the same, because of the low deuterium content. The measured shift of the distillate gives directly the equilibrium constant of the reaction, $RT\ \ln\frac{p_{HDO}}{p_{H_2O}}+\text{const.}$ The heat toning of the reaction or the difference between partial molar heat of vaporisation for HDO and H_2O was calculated from the temperature variation of the equilibrium constant as −215 ±24 calories.

The heat toning of the reaction might also be correlated with spectroscopic data. We assumed that the rotational energies are fully excited at the temperatures, that the rotational degree of freedom in liquid phase is exactly the same for HDO_{liq} and for H_2O_{liq} and that vibrational energies are at their lowest quantum states both for single molecule and for polymers in the liquid. The heat toning Q is then given by the difference of zero point energies of aggregates,

$$Q=\frac{1}{2}\sum h\nu_{H_2O_{vap}}+\frac{1}{2}\sum h\nu_{HDO_{liq}\text{-}xH_2O_{liq}} -\frac{1}{2}\sum h\nu_{HDO_{vap}}-\frac{1}{2}\sum h\nu_{H_2O_{liq}\text{-}xH_2O_{liq}} ,$$

where νs means fundamental vibrational frequencies. Fundamental frequencies were given for H_2O_{vap} and HDO_{vap} by Bartholomé and

Clusius,(3) and by Wood,(4) and for liquid by Ellis and Sorge.(5) Ellis and Sorge assume the fourth fundamental frequency ω^* for polymerisation and give 2130 cm.$^{-1}$ for H_2O and 1640 cm.$^{-1}$ for D_2O. Should Q by the above expression give the measured heat toning taking ω^* into account, lacking data of ω^* for HDO would be 1740 cm.$^{-1}$, which lies between those for H_2O and for D_2O. The expression for Q would give positive value +300 cals. without taking ω^* into consideration, in contrary to the measured endothermicity of the reaction.

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(3) Bartholomé and Clusius, *Z. Elektrochem.*, **40** (1934), 529.
(4) Wood, *Phys. Rev.*, **45** (1934), 732.
(5) Ellis and Sorge, *J. Chem. Phys.*, **2** (1934), 558.