

Isotopic Exchange Equilibria

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The utility of isotopic exchange equilibria in accounting for various other equilibria in light-heavy water mixtures has been shown previously by the author.¹ The present work is an attempt to measure reliably some of these exchange equilibria by means of an improved technique, of which the essential improvement over earlier work² is the substitution of the immersed float for the pycnometer and the ability to carry out all operations in vacuum.

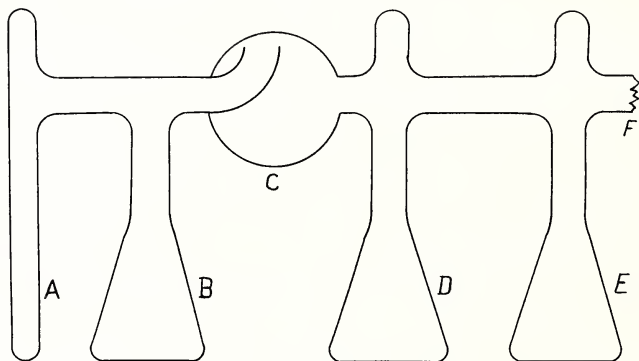


Fig. 1

About one gram of water (16% D_2O or 32% D_2O), which just fills a small ampoule with capillary stem, is weighed in the sealed ampoule and introduced into E (Fig. 1). The substance for exchange is weighed in a small open tube and introduced into D. The float is placed in A, the openings to A, D, and E sealed and D warmed on a water bath while the vessel is evacuated and then sealed at F. The water is liberated by immersing E in dry ice-ether, distilled into B, then poured into A and the density determined; the water is rinsed into C, distilled back to B, etc., and the density redetermined. The water is then distilled into the substance in D, and from D to E to B and the density again determined. This series of distillations is repeated as check.

The temperature is controlled by a glass-walled thermostat constant to $\pm 0.001^\circ$ and temperature differences observed on a Beckmann thermometer calibrated against one with Bureau of Standards certification. A cathetometer is employed for observations of thermometers and floats.

The densities of the floats were determined with reference to potassium chloride solutions whose densities were measured with 25 cc.

¹ Hamill, 1937. *Journ. Amer. Chem. Soc.* 59:1492.

² Hamill and Freudenberg, 1935. *Journ. Amer. Chem. Soc.* 57:1427.

pycnometers and were reproducible to ten parts per million. Calibrated weights were employed and buoyancy corrections applied.

Quartz floats were used, and the temperature of the water adjusted at practically constant pressure (the vapor pressure of water) until flotation equilibrium was reached. Since floats have been employed at constant temperature and varying pressure, it is appropriate to remark that the floats employed here had apparent coefficients of compressibility, referred to water, of about $2(10)^{-5}$ per atmosphere. Since the velocity of the float altered by $0.03 \text{ cm./sec./1}^\circ$, it was readily possible to detect differences in density of one part per million.

Blank runs showed that a negligible amount of atmospheric moisture was adsorbed on the glass walls of the vessel and that spattering, volatility of substance or hydrolytic products and reproducibility of measurements did not affect the density of water by more than one part per million except for hydroquinone which had a slight effect.

TABLE I.

Substance	K (16%)	K (32%)	K (0%)	K (calc.)
$\text{CO}(\text{NH}_2)_2$	0.609	0.614	0.60	0.35
NaOH	0.484	0.578	0.39	
KHSO_4	0.371	0.440	0.30	
KH_2PO_4	0.354	0.372	0.33	
$\text{C}_2\text{H}_4(\text{COOH})_2$	0.572	0.632	0.51	0.55
$\text{p-C}_6\text{H}_4(\text{OH})_2$	0.590	0.632	0.55	

The experimental results are summarized in Table I. A considerable discrepancy is observed between the equilibrium constants at 16% D_2O and at 32% D_2O , this constant being defined by the equations:

$$\text{RH} + \text{HDO} = \text{RD} + \text{H}_2\text{O}$$

$$(\text{H}_2\text{O})(\text{RD})/(\text{HDO})(\text{RH}) = K$$

where RH is the equivalent of substance with respect to exchanging hydrogen, e.g. $\frac{1}{2} \text{C}_6\text{H}_4(\text{OH})_2$. The observed discrepancies may be due to any or all of the following: (1) fractionation of the water upon distillation and a continuous series of equilibria with the substance in the process of crystallizing from solution, (2) failure of the assumption that in molecules containing two or more hydrogen atoms there is no effect upon other positions due to exchange in any given position, and (3) differences in solubility of RD and RH in the different heavy water mixtures. The first possibility is readily tested, and it was found, by experiments which will not be reported here in detail, that there is no significant trend in K for hydroquinone and succinic acid when up to 90% of these substances is crystallized from solution, by saturating at 100°C. and cooling to 25°C. , before distillation begins. The second possibility may be eliminated by extrapolating K to zero per cent heavy

water, which also eliminates the effects of HDO and D₂O upon solubilities, while the differing solubilities of RD and RH in any given aqueous medium are not susceptible to measurement and must remain as an unknown and possible source of error. The extrapolated constant is given in the table as K (0%) and may be compared, in two instances, with indirectly obtained constants.³ Earlier measurements of K for hydroquinone, by the author, have been employed by Korman and LaMer,⁴ in conjunction with their measurements on the quinhydrone electrode, to calculate several important equilibrium constants. The value of K for hydroquinone reported here is in essential agreement with the earlier measurement.

Summary

Isotopic exchange equilibrium constants have been measured by means of an improved technique for several substances at two concentrations of heavy water. Factors affecting their reliability are pointed out.

³ Hamill, 1937. Journ. Amer. Chem. Soc. 59:1492.

⁴ Korman and LaMer, 1936. Journ. Amer. Chem. Soc. 58:1936.