the order of magnitude of L seems beyond experimental accessibility.

Because ${}^0k_q(1 - \beta')$ and ${}^0k_q a$ are both virtually independent of σ, it does not appear that any information about detailed microscopic behavior in liquids is obtainable from kinetic measurements on reactive molecules that are produced singly. The best hope for obtaining such information continues to lie with situations in which reactive species are produced in pairs.[2,7]

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[7] R. M. Noyes, THIS JOURNAL, 77, 2042 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE]

The Equilibrium Distribution of Light and Heavy Waters in a Freezing Mixture

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The equilibrium distribution of the deuterium content of a mixture of light and heavy water between the solid and liquid phases has been determined. The deuterium concentrates in the ice phase. The separation factor, α, in solutions containing approximately 18 mole % of the total hydrogen as deuterium was found to be 1.0211 ± 0.0007.

Since the freezing point of pure heavy water is 3.80° higher than that of ordinary water,[1,2] it might be expected that a partial separation of the two isotopic hydrogen species could be accomplished by freezing. This observation has led to several investigations, with varying results. Bruni,[3] Chang,[4] Dezelic,[5] and La Mer, Eichelberger and Urey[6] report that no measurable separation occurs. Gilfillan[7] reported enrichment of deuterium in the ice phase when natural water was partly frozen. Teis and Florensky[8] reported enrichment of deuterium in the liquid phase under similar circumstances. However Teis[9] later stated that these results were in error, and reported that when snow melts, the deuterium is concentrated in the ice phase.

La Mer and Baker[10] and Eucken and Schaefer[1,2] calculated the equilibrium concentrations of deuterium in the ice and water phases. The values of the separation factor calculated from the data of those investigators at deuterium concentrations near those of this work (approximately 20%) were 1.040 and 1.023, respectively. Both of the groups of investigators used indirect methods of experimental verification. These calculations have apparently never been verified by direct measurement of the isotopic compositions of the two phases.

The very slow rate of diffusion of water molecules in the liquid phase causes true equilibrium separation to be difficult to obtain. According to Wang, Robinson and Idelman,[11] the diffusion coefficient of HDO in water is only 1.57×10^{-5} cm.^{2} sec.$^{-1}$ at 10°, and decreases as the temperature is lowered. As ice crystals grow in a freezing mixture, the water adjacent to their surface becomes depleted in deuterium as compared to the bulk of the liquid, and the concentration of deuterium in the ice formed will correspond to this reduced concentration. Therefore, the observed separation, as based on the bulk composition of the phases, will be less than the true value. This effect can be reduced by the use of vigorous agitation and very slow freezing rates.

Even with vigorous agitation a layer of water will remain motionless at the ice–water interface. As the distance from the solid increases the motion of the liquid increases so that this layer has no definite outer boundary. However, for purposes of mathematical analysis the film may be considered to be equivalent to a film of a definite thickness, B. This assumption is often made in engineering calculations.[12]

The true separation factor α_0, and the observed separation factor, α, are defined by the equations

$$\alpha_0 = \frac{y(1 - x^1)}{x^1(1 - y)} \tag{1}$$

and

$$\alpha = \frac{y(1 - x)}{x(1 - y)} \tag{2}$$

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[1] A. Eucken and K. Schaefer, *Z. anorg. allgem. Chem.*, **225**, 319 (1935).

[2] A. Eucken and K. Schaefer, *Nachr. Ges. Wiss. Gottingen, Math.-physik. Kl., Fachgruppe III*, **I**, 109 (1935).

[3] G. Bruni, THIS JOURNAL, **56**, 2013 (1934).

[4] T. L. Chang, *Ber.*, **69B**, 1302 (1936).

[5] M. Dezelic, *Bull. soc. chim. roy. Yougoslav.*, **7**, 65 (1936).

[6] V. K. La Mer, W. C. Eichelberger and H. C. Urey, THIS JOURNAL, **56**, 248 (1934).

[7] E. S. Gilfillan, *ibid.*, **56**, 2201 (1934).

[8] R. V. Teis and K. P. Florensky, *Compt. rend. acad. sci. U.R.S.S.*, **32**, 199 (1941).

[9] R. V. Teis, *ibid.*, **53**, 529 (1946).

[10] V. K. La Mer and W. N. Baker, THIS JOURNAL, **56**, 2641 (1934).

[11] J. H. Wang, C. V. Robinson and I. S. Idelman, *ibid.*, **75**, 446 (1953).

[12] W. L. Badger and W. L. McCabe, "Elements of Chemical Engineering, McGraw-Hill Book Co., Inc., New York, N. Y., 1936, p. 246.

where y is the deuterium mole fraction in the ice phase at the interface, x' is the deuterium mole fraction in the water phase at the interface, and x is the deuterium mole fraction of the bulk of the liquid.

As the ice–water interface moves into the liquid due to freezing, this layer moves along ahead of it. If the rate of freezing is $\mathrm{d}m/\mathrm{d}t$, the rate at which deuterium leaves the layer is $y(\mathrm{d}m/\mathrm{d}t)$ and the rate at which it enters the layer due to the advance of the film is $x(\mathrm{d}m/\mathrm{d}t)$. The difference, $(y - x)\cdot \mathrm{d}m/\mathrm{d}t$ must equal the rate of diffusion across the layer, or

$$(y - x)\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{DA(C_1 - C_2)}{B} \qquad (3)$$

where D is the diffusion coefficient, A is the area over which diffusion occurs, B is the thickness of the layer through which diffusion occurs, and C_1 and C_2 are the deuterium concentrations in the liquid phase at the two edges of the film. If the rate is expressed in moles per second, the concentrations can be expressed as mole fractions with the insertion of the constant, S, the total number of moles per unit volume.

$$(y - x)\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{DAS}{B}(x - x') \qquad (4)$$

When x' is nearly the same as x, it follows from eq. 1 and 2 that

$$\frac{\alpha_0 - 1}{\alpha - 1} = \left(\frac{y - x'}{y - x}\right)\frac{x}{x'} = \frac{y - x'}{y - x} \qquad (5)$$

By eliminating x' from eq. 4 and 5, eq. 6 is obtained.

$$\frac{\alpha_0 - 1}{\alpha - 1} = \frac{B}{DAS}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) + 1 = C\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right) + 1 \qquad (6)$$

Since the temperature varies only about 0.02° during the course of a test D and S can be considered to be constant. Both A and B may vary to some extent during the course of the test due to the growth of the ice phase. However, when a series of tests is carried out with little change in conditions other than freezing rate, C may be treated as a constant. When $\mathrm{d}m/\mathrm{d}t$ approaches zero, α approaches α_0.

Experimental Procedure

Two preliminary tests were performed in which the water was frozen rapidly without agitation. In these tests 10-ml. glass stoppered flasks containing the isotopic water mixture were placed beside a lump of Dry Ice in a large Dewar flask. When somewhat more than half of the water had frozen the water phases were poured away from the ice. Both phases were analyzed for deuterium content.

More accurate tests were carried out in a flask equipped with a vacuum jacket which was evacuated thoroughly at 400° with a mercury diffusion pump and permanently sealed. A small amount of metallic sodium was enclosed in the jacket as a "getter."

The freezing was accomplished by the immersion of the vacuum jacketed flask containing the sample in a mixture of ordinary ice and water contained in a Dewar flask. This caused a nearly constant temperature difference to be maintained between the freezing sample and outside of the flask. Since the samples used in this work contained about 18 mole % deuterium, the temperature difference was 0.7° when the outer Dewar flask contained pure water and ice. Higher freezing rates were obtained by mixing various sparingly soluble salts in excess with the ice and water.

The sample flask was held firmly in place in the Dewar flask by means of a piece of heavy walled rubber tubing wedged between the wall of the Dewar flask and the sample flask, and by a cork collar. This collar insulated the top of the ice-bath, and assured a constant temperature gradient in the upper part of the flask.

The Dewar flask was mounted in a mechanical shaker which moved the flask back and forth in a horizontal plane over a distance of two inches. Shaker speeds of 200 to 225 cycles per minute were used. Higher speeds caused the formation of slushy ice.

The isotopic water mixture was prepared by mixing 99.8% heavy water from the Stuart Oxygen Company with laboratory distilled water. The samples consisted of 5-ml. portions of this water. They were boiled under vacuum to remove dissolved gases and were distilled under vacuum into the sample flask. The vapor was passed through a glass wool plug to remove any entrained material.

The presence of seed crystals was found to be necessary to prevent supercooling. These were formed by immersing the sample flask in a mixture of Dry Ice–acetone until freezing was observed. The flask was then held at room temperature until the ice had just melted and was again immersed in the Dry Ice–acetone mixture for three to four minutes. It was then removed and shaken vigorously. This caused a light film of ice crystals to form on the walls of the flask. The samples were shaken in the ice-bath for periods of time that varied from 4 to 46 hours depending on the rate of freezing.

At the end of the test the water was drained from the ice by the following procedure. A small container was connected to the sample flask by means of the ground glass joint. This container was evacuated through a side tube equipped with a stopcock. After evacuation this stopcock was closed and the container was disconnected from the vacuum line. The container, sample flask and ice-bath were then inverted together and immersed in a large beaker of ice and water. The stopcock on the sample flask was then opened and the water allowed to drain into the container. Since the vessel which received the liquid sample was slightly cooler than the sample no refluxing of the water occurred during the transfer. The weights of the ice and water phases were determined from the weights of the flask when full, after removal of the water phase, and the tare weight.

The deuterium concentrations of the two phases were determined by the falling drop method of analysis. The apparatus and procedure have been described by Combs, Googin and Smith.[13]

The separation factor, α, has been defined as the ratio of the molar ratio of deuterium to hydrogen at the surface of the ice phase to the similar molar ratio in the water phase. It was assumed that diffusion within the ice phase was negligible and that the liquid phase became progressively depleted in deuterium as freezing proceeded. This situation is analogous to Rayleigh distillation.[14] The apparent separation factor, α, was calculated from eq. 7.

$$\alpha \log\left(1 + \frac{m(1 - y)}{M(1 - x)}\right) = \log\left(1 + \frac{my}{Mx}\right) \qquad (7)$$

Here, M is the total number of moles in the water phase, m is the total number of moles in the ice phase, x is the mole fraction of deuterium in the water phase, and y the mole fraction of deuterium in the ice phase.

Results

The values of α calculated from the results of the tests with comparatively rapid freezing without agitation were 1.0007 and 1.002. These values were obtained at freezing rates of 11 and 4 g. per hour, respectively.

A number of badly scattered values of the separation factor were obtained during the development of the technique of measurement. It was ascertained that these variations were caused by changes in the depth of immersion of the flask during the run and the consequent remelting of parts of the ice phase. This destroyed the relationship given

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(13) R. L. Combs, J. M. Googin and H. A. Smith, *J. Phys. Chem.*, **58**, 1000 (1954).

(14) J. H. Perry, "Chemical Engineers Handbook," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 1383.

by eq. 7. This trouble was corrected by the use of the cork collar which has been described.

In other tests the ice did not form a uniform film on the walls of the flask. Shaker speeds much above 200 cycles per minute caused the formation of free floating slush. Freezing rates much below 0.1 g. per hour resulted in every case but one in the formation of pellets of ice. The values of the separation factor obtained from these tests were consistently lower than those obtained when the ice was in the form of a uniform film. They varied from 1.0145 to 1.0183.

The final values of the separation factor which were obtained after the technique was developed are given in Table I. This table includes the freezing rates, the per cent. of each sample frozen, and the isotopic compositions of the phases.

A value of 1.0211 ± 0.0007 for the separation factor at zero freezing rate was obtained by means of a least mean square plot of $1/(\alpha - 1)$ as a linear function of the freezing rate, $\mathrm{d}m/\mathrm{d}t$. Equation (8) was obtained

$$\frac{1}{\alpha - 1} = 17.81 \frac{\mathrm{d}m}{\mathrm{d}t} + 47.33 \qquad (8)$$

All of the data of Table I were used in this extrapolation except the value at 0.05 g. per hour. This slow rate had been obtained by reducing the depth of immersion of the sample flask in the ice–water mixture. This resulted in the formation of an ice film only on the bottom part of the flask. This film was visually estimated to have about one-third the area of the other films. The probable error, 0.0007, was calculated from the deviation of points from the line of eq. 7 by the method of Fisher,[15] and from the uncertainty of the calibration of the reference solution used in the isotopic analysis.

TABLE I

THE SEPARATION OF HYDROGEN AND DEUTERIUM BY THE FREEZING OF WATER

Freezing rate, g./hr.	Mole % deuterium		Wt. % frozen	α
	Ice phase	Water phase		
0.050	18.211	17.832	45.1	[1.0195]
.096	18.332	17.846	61.2	1.0213
.100	18.328	17.885	53.1	1.0211
.157	18.308	17.963	33.8	1.0192
.227	18.180	17.818	39.6	1.0194
.323	18.231	17.906	37.7	1.0176
.560	19.579	19.205	48.8	1.0176
.598	17.533	17.158	57.3	1.0177

Discussion

The very low separation obtained without agitation and at relatively high freezing rates shows the importance of these factors. Thermal convection undoubtedly caused some mixing of the water phase during freezing. Otherwise, even less separation would have occurred.

Two small systematic errors probably occurred in all of the determinations of this work both of which tend to cause the measured values of α to be smaller than the true value. When the water was drained from the ice phase a thin film must be assumed to have remained behind on the surface of the ice and the walls of the flask. However, the amount of this water and the resulting error was, at worst, small. The ice seed crystals, whose presence was necessary to start freezing, were formed under conditions of very rapid freezing and probably contained less than the equilibrium concentration of deuterium. Since the amount of this ice was small the resulting error could not have been great. It is also possible that part of this ice melted, the heat of fusion being furnished by the freezing of ice of a higher deuterium content.

The error due to fractionation of oxygen isotopes is negligible. Analysis by mass spectrometer of the ice and water phases from one of the tests of this work was performed by the Oak Ridge National Laboratory. The oxygen 18 isotope concentrations were 0.230 ± 0.001 and 0.230 ± 0.002%. The maximum error in both analyses would have caused an error of only 0.0003 in α.

A separation of oxygen isotopes during the freezing of water was reported by Teis and Florensky.[8] However, Teis[9] later reported these data to be in error.

The value of 1.0211 ± 0.0007 obtained in this work is in fair agreement with the value of 1.023 calculated by Eucken and Schaefer.[1,2] The previously discussed systematic errors may account for part of the difference.

The value of α calculated from the calculated phase concentrations of La Mer and Baker[10] is 1.040. These workers assumed that only two molecular species, H_2O and D_2O, were present. An approximate calculation made with the assumption that three species, H_2O, HDO and D_2O, exist in equilibrium, give a value of 1.020 which is close to the experimental value.

Chang[4] used very high freezing rates in his work. This accounts for the fact that he observed no separation.

Dezelic[5] concluded that no separation occurred from the fact that, according to his measurements, the freezing point of water was a linear function of the deuterium concentration. However, as pointed out by Eucken and Schaefer[1] his measurements were not sufficiently precise to detect the departure from linearity which does occur.

The reasons for the failure of other investigators are not clear. La Mer, Eichelberger and Urey[6] were interested chiefly in a large separation such as might occur if the two isotopic species did not form an ideal solution in the solid phase.

Acknowledgment.—The authors are indebted to the United States Atomic Energy Commission for support of this work.

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(15) R. A. Fisher, "Statistical Methods for Research Workers," 11th Edition, Oliver and Boyd, London, 1950, p. 135.