



Fig. 2. Projections of flocs simulated using simple Smoluchowski model.

the absence of any directional mechanism in the simulation model.

The results suggest that chain formation is not nearly as unlikely a phenomenon as might at first be expected. When one considers that the number of primary particles which are observed when looking at aggregates probably runs into thousands, it is not at all improbable that many chains of around ten particles are present. Growth kinetics which favour cluster addition will accentuate the effect, and in general this seems most likely in aerosol systems at high Knudsen number (ratio of molecular mean free path length to particle radius). In these conditions the simple Smoluchowski perikinetic rate equation, in which collision rate is independent of particle size, is replaced by the free molecule kinetic expression predicting a collision rate proportional to the square root of the particle size⁷.

It must be remembered that a rigid bond has been assumed throughout. Any flexibility in the link will greatly reduce chain formation.

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Fractionation Factor of ¹⁸O between Water Vapour and Ice

FOLLOWING investigations by Jancso *et al.*¹ of the vapour pressure of H₂¹⁸O ice between -17° and 0° C, I have measured the fractionation factor of ¹⁸O between water vapour and ice from -33.4° to 0° C. The method derives from the "steady state method" first applied by Boato *et al.*² to argon isotopes. Our experimental procedure is similar to that described by Merlivat and Nief³ for the deuterium fractionation factor (H₂O-H₂HO) between

water vapour and ice. Using a mass spectrometer⁴ specially designed for analysis of the isotopic ratio $R = (H_2^{18}O)/(H_2^{16}O)$ by direct injection of water vapour into the apparatus, we can measure directly the fractionation factor $\alpha = R_s/R_v$, where R_s and R_v are the ¹⁸O isotopic ratios for ice and water vapour respectively. The apparatus measures α to an accuracy of $\pm 10^{-4}$.

Our results can be represented by the relationship

$$\ln \alpha = \frac{11.839}{T} - 28.224 \times 10^{-3}$$

The standard deviation between calculated and experimental values is $\pm 3 \times 10^{-5}$ for $\ln \alpha$. Assuming the validity of Raoult's law for the temperature range studied here, one can write $\alpha = p_{H_2^{18}O}/p_{H_2^{16}O}$. Table 1 compares our results with those of Matsuo and Matsubaya⁵ and Jancso *et al.*¹.

Table 1. NEW VALUES FOR α COMPARED WITH THOSE OF REF. 5 (M. M.) AND REF. 1 (J. P. V.)

t (°C)	M. M.	$10^3 \ln \alpha$ J. P. V.	Our results
0	11.5	14.3	15.1
-5	11.8	14.4	15.9
-10	12.2	14.6	16.8
-17	12.7	14.8	18.0

Systematic measurements of the ¹⁸O fractionation factor between water and water vapour from 0° to 90° C have been made by sampling water vapour from a liquid-vapour equilibrium. Our results are in good agreement with those of ref. 6 and with the relationship of ref. 7. The ¹⁸O fractionation factor between ice and water at 0° C deduced from our results is given by $\ln \alpha_{ice-water} = 0.0034 \pm 0.0003$. This value agrees with O'Neil's⁸ directly measured value of 0.0030 ± 0.0002 .

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Proton Hyperfine Coupling Constants in Radicals and the Effect of Orbital Overlap

RECENTLY Symons¹ has considered the influence of the excess charge effect on proton hyperfine coupling constants. He observed that cations always seem to have larger proton hyperfine coupling constants than the analogous anions. This was rationalized as the systematic changing of the effective nuclear charge on the proton with the excess charge on the radical. The series of iso-electronic radicals BH₃⁻, CH₃ and NH₃⁺ was used to demonstrate the principle very convincingly.

The purpose of this note is not only to provide theoretical evidence for the excess charge effect but to show that if other effects are ignored, for example, orbital overlap and bond length, the excess charge effect is attenuated. The extent of the attenuation does not seem to be sufficient to justify exclusion of the excess charge effect from semi-empirical theories which ignore all of these effects, for example, INDO (ref. 2).