

Letters to the Editor

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NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 1042.

CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

What is a Colloid?

ASSOCIATION is the characteristic factor in the colloidal state.

Without it, no films, fibres, glasses, resins or plastics, no jellies, gels, liquid crystals, coagula or gelatinous precipitates, no high viscosity (Graham's colloidoscope), no opalescence, no colloidal particles built up of a myriad of ordinary atoms or molecules, no electrosmosis or streaming potential, no membrane equilibrium or any of the effects defined by Loeb as 'colloidal behaviour', no stabilising agents or protective action or sensitisation, no stability however transient of the great majority of colloidal particles which are dependent upon structural arrangement, not even the folding of the long chain molecules that gives the characteristic properties to such colloids as wool or rubber; none of the beautiful and varied architecture which utilises as building stones the colloidal particles, which are themselves products of association.

In recent years there has been a tendency, particularly on the part of some who have been emphasising the immensely long chain structure of certain natural and synthetic colloids and their relation to viscosity in very dilute solution, to do away with the term micelle and to think only of the individual molecule as a single simple kinetic unit. However, since the convincing work of Sponsler, Dole, Meyer, Mark and Staudinger, no one now questions the long chain nature of such molecules as cellulose.

Soaps are still recognised as association colloids, and the association of their molecules and ions is known to produce particles of orderly structure. Yet this distinction is incompletely valid, for in dilute solution, to which Staudinger's formulations are confined, soaps are not colloids at all. As a matter of principle, in sufficient dilution in a suitable medium, all colloids are resolved into their molecular or ionic constituents, as happens with sols of WO_3 and V_2O_5 . Few would care to deny association in higher concentrations, but are we to assume that in contrast to soaps or suspensions the association of long chain molecules is wholly disordered?

Whereas in dilute solution simple sulphonic acids, as will be shown in a series of articles elsewhere, consist of ordinary molecules and ions, in concentrations above $N/10$ association is so predominant as wholly to submerge the influences discussed in the ionic attraction theory. The result is that effects such as conductivity, freezing point lowering, and electromotive force increase instead of decreasing with concentration. Association must be of the cohesive van der Waals' type, emphasising the principle of 'like to like'.

When association is so predominant in such simple cases, it must be important in the behaviour of chain molecules, and indeed must be a factor always to be reckoned with in all solutions.

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Stanford University,
California. May 22.

Raman Spectra of Deuterobenzenes and the Structure of Benzene

THE letter by Klit and Langseth in NATURE of June 8 (p. 956), recording Raman frequencies of some deuterobenzenes, leads us to report our own results so far as these overlap, although we had wished to reserve publication until the problem of which these spectra supply only part of the answer had been fully solved. Klit and Langseth record 8 lines for C_6D_6 , and 1 for each of C_6H_5D and C_6HD_5 (not obtained pure). This note relates to C_6D_6 and C_6H_5D (both pure); we have not prepared C_6HD_5 ; we have, however, examined 1:4- $C_6H_4D_2$ and hope to study 1:3:5- $C_6H_3D_3$ also, for the following reason.

An acute problem concerning the structure of benzene was raised when Placzek showed¹ that the same fundamental frequencies cannot appear in both the Raman and infra-red spectra of molecules possessing a centre of symmetry. Bhagavantam² and Krishnamurti³ had directed attention to several apparently coincident frequencies in these two spectra for benzene, and this seemed to show that benzene has not the plane regular hexagonal structure (point group D_{6h}) which the resonance theory requires. Various models of lower symmetry have been suggested by Placzek himself, and by Cabannes and Rousset⁴, Deitz and Andrews⁵, Weiler⁶ and others. One model of sufficient dissymmetry is the static Kékulé structure, but to revert to this would be retrograde on other grounds. The difficulty would disappear, however, if it could be shown that the coincidences are accidental, that is, that the identical or nearly identical frequencies depend in fact on different proper vibrations. The problem is therefore to identify the proper vibrations, and this we shall do by measurement of the H-D displacements, first when the total symmetry of benzene is maintained as in C_6D_6 , and secondly when different elements of symmetry are removed, as in 1:3:5- $C_6H_3D_3$, 1:4- $C_6H_4D_2$ and C_6H_5D . At present we are studying the Raman, infra-red and ultra-violet spectra of C_6D_6 , 1:4- $C_6H_4D_2$ and C_6H_5D .

	C_6H_6	C_6D_6		C_6H_5D	
	Literature	This Note	K. and L.	This Note	K. and L.
(i)	607 (3)	583 (3)	582	609 (3) 785 (1)	—
(ii)	849 (1)	666 (3)	845	855 (1)	—
(iii)	993 (10)	944 (10)	947	984 (10)	982
(iv)	1176 (3)	867 (3b)	870	1175 (5)	—
(v)	{ 1585 (3b) 1606 (1)	{ 1536 (3b) 1566 (3b)	{ 1555 1569	1597 (5b)	—
(vi)	3049 (2)	2265 (3)	2267	{ 2271 (2)	—
(vii)	3064 (5)	2292 (5)	2292	{ 3059 (10b)	—

Our Raman frequencies for C_6D_6 and C_6H_5D are in the accompanying table; approximate intensities are given in parenthesis, but not polarisations, as these measurements are not yet complete. The