THOMAS GRAHAM AND THE DEFINITION OF COLLOIDS

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At present we have two definitions of colloids. The 'founder of colloid chemistry', Thomas Graham[1], one hundred years ago, defined the colloids as substances of complicated chemical nature with very high molecular weight and a specific structure of molecules. Owing to this fact the molecules of colloids possess the properties different from those of crystalline bodies or crystalloids. But Graham emphasized that the process of solution of colloids, that is, the formation of solutions and the phenomena which accompany them, differ from those of crystalloids only in degree. The solution of colloids is very slow and the change of temperature is barely perceptible. Graham defined the colloidal state as a dynamical state of matter which may change into a crystalloidal statical condition. The colloidal state of matter possesses *energia*, and Graham suggested that the phenomena associated with life in those bodies which consisted almost wholly of colloids is due to that *energia*.

The world of colloids is particularly the world of organic high-molecular substances; however, Graham showed that inorganic substances composed of molecules of high molecular weight and complicated structure can be also obtained in colloidal state. The solutions of colloids are real solutions and they obey the laws of physical chemistry and thermodynamics. According to Graham the colloidal state of substances is determined by the high molecular weight.

In his papers Graham does not mention the investigations of Faraday[2] on the finest suspensions of metallic gold, nor the works of Selmi[3] on pseudo-solutions. The finest suspensions of gold and pseudo-solutions of Selmi are not real solutions but micro-heterogeneous systems. Graham, in agreement with his conception of colloids, never assumed that the finest suspensions of gold, silver chloride, sulphur and other similar systems are colloidal solutions.

But about half a century after the establishment of colloid chemistry by Graham, a new definition of colloids was proposed by Freundlich, Wo. Ostwald and Weimarn[4] which did not conform with that given by Th. Graham. These scientists proposed to call any substance which is in the dispersed state 'colloidal'. The molecular weight of the dispersed substances had no relation to the colloidal state by that definition. The finest suspensions or emulsions of dispersed substances in a medium were colloidal solutions according to them.

Graham would not have considered the solutions of Freundlich, Ostwald and Weimarn as real solutions but as microheterogeneous (dispersed) systems. This second definition of colloids was accepted by most scientists and the finest suspension of gold was considered as a typical colloid[5].

Meanwhile, it is necessary to recall that Graham chose gelatin as the prototype of colloid[6].

The difference between the points of views of Graham and the later three authors as to the question of what the typical colloid is, is evident.

Those who supported the dispersoid conception as an explanation of the behaviour of Graham's colloids (high-molecular substances) in solutions, ascribed much greater hydration to them than could be proved by experiment[7]. Since Staudinger[8] introduced the conception of 'macromolecule', some scientists[9], fortunately only very few, proposed not to consider the colloids of Graham as colloids, but to refer to them only as high-polymers because these substances made real solutions but by no means microheterogeneous (dispersed) systems.

However, it will be noted again that Graham always considered the colloidal solutions as real solutions and never as the pseudo-solutions or microheterogeneous systems. But both these definitions of colloids may be reconciled if we assume, with Perrin[10], the definition of 'gigantic physical molecule', which in its physical and thermodynamic behaviour has no distinction from the behaviour of chemical molecules. Therefore we may regard the finest suspensions of those particles which show Brownian movement and obey the laws of kinetic theory of heat as real solutions. Einstein[11], Perrin[10], Svedberg[12] and Smoluchowski[13] proved this conception to be true by theoretical and experimental investigations.

Thus we may conclude that modern colloid chemistry is the physical chemistry of gigantic physical and chemical molecules.

[1] Graham, Th., *Phil. Trans. Roy. Soc.*, **151**, 183, 184, 206, 207, 220 221 (1861).
[2] Faraday, M., *Phil. Trans. Roy. Soc.*, 145 (1857).
[3] Selmi, F., Ostwald's *Klassiker der exakten Wissenschaften*, 217; *Klassische Arbeiten über Kolloide Lösungen*, 135, 147 (Leipzig, 1926).
[4] Freundlich, H., *Kapillarchemie*, **1**, 1 (Leipzig, 1930). Ostwald, Wo., *Kolloidchem. Beih.*, **4**, 9 (1912). Weimarn, P. P., *ibid.*, **2**, 401 (1911).
[5] Zsigmondy, R., *Kolloid Zhur.*, **26**, 1 (1920).
[6] Graham, Th., *Phil. Trans. Roy. Soc.*, **151**, 183 (1861).
[7] Kargin, V. A., and Slonimskii, G. L., *Short Sketches of the Physical Chemistry of Polymers*, 10 (Moscow Univ. Ed., 1960).
[8] Staudinger, H., *Ber.*, **53**, 1073 (1920).
[9] Voyutskii, S. S., *Kolloid Zhur.*, **23**, 354 (1961).
[10] Perrin, J., *Kolloidchem. Beih.*, **1**, 262 (1909–10).
[11] Einstein, A., *Ann. d. Phys.*, **17**, 549 (1905).
[12] Svedberg, T., *Die Existenz der Molekule*, 64 (Leipzig, 1912).
[13] Smoluchowski, M., *Ann. d. Phys.*, **21**, 756 (1906).

UNIVERSITY ENTRANCE REQUIREMENTS IN ENGLAND AND WALES

In March 1960 the Committee of Vice-Chancellors and Principals set up a sub-committee, including a substantial proportion of university teachers, to report on university entrance requirements, and the preliminary report of this sub-committee in March 1961 satisfied the Vice-Chancellors and Principals that the time was opportune for a careful reconsideration of entrance requirements by the universities. When the draft report was circulated as a confidential document to the universities for comment, there was

an almost uniformly favourable response to the proposal for some alignment in form and approximation in substance of present entrance requirements. The Committee of Vice-Chancellors and Principals has accordingly asked universities forthwith to restate their present requirements in a common form, and at the same time, where possible, to bring them closer into line when they differed in substance.

This restatement is now being carried out, with a view of publication in a combined volume before the end of this year. A second main proposal of the draft report*, a new pattern of entrance requirements, was put forward as an educational reform, and after careful examination, Cambridge, London and Reading expressed opposition in principle. Oxford has not yet given any opinion, but the remaining universities approved or welcomed the idea of the proposal, and comments offered were directed to modifications of detail. The Committee of Vice-Chancellors and Principals judged, therefore, that there was sufficient university support to justify the wider discussion of the proposal, and its publication was authorized in this report after redrafting to meet most of the points raised in the detailed comments.

The report opens with a brief historical review of the development of university entrance requirements in England and Wales in their present form over the past sixty years or so, and this is followed by an analysis of the present difficulties arising from variations and ambiguities in the method of statement of entrance requirements by universities, variations in the entrance requirements themselves, whether in subjects named or in the numbers of subjects in which passes are required, or from the weakness of the general pattern of entrance requirements.

The first proposal, already being implemented, is that all universities in England and Wales should publish their examination requirements for entry on first-degree courses in a common form, using standard terms. In this common form the terms 'matriculation requirement' and 'minimum entrance requirement' are replaced by the term 'general requirement', to denote the group of required passes at both levels in the General Certificate of Education, examination equivalent to what is now demanded for Matriculation. Similarly, the term 'course requirement' is proposed in place of 'faculty requirement' and 'department requirement' to denote the group of required passes at both levels in the General Certificate of Education examination equivalent to what is now asked for entry into specified faculties or departments, and this Course requirement should be stated in terms of numbers and names of subjects in which 'normally' a candidate should have passed, to hope to be academically acceptable to the department or university concerned. As already indicated, the proposal contemplates that each university will print and publish its entrance requirements for first-degree courses in single joint annual volume.

The second proposal is more far-reaching and radical, and the Committee believes that adoption of this proposal would not only automatically remove some of the formidable difficulties for candidates which now arise from the interlocking of the minimum entrance requirements and the faculty and department requirements, in terms of General Certificate of Education subjects at both levels, but by placing more weight than hitherto on general studies than special studies in the sixth form, could permit an educational improvement of considerable benefit both to universities and to schools. The present balance between general and special studies is the result of piecemeal adjustments made over a long period as conditions in the schools and universities have slowly changed and as the structure of public examinations has been altered. Tacitly abandoning their former requirement of a broad intellectual training alone as a condition of entry, the universities have substituted for it a primary demand for competence in subjects of special study, and evidence of general education has become a secondary requirement, the test for which is made at the beginning of the sixth-form course. The essential new feature of the proposed new pattern is that it recognizes the importance of general studies in the sixth form by making them examinable, just as are the subjects of special study.

The essence of the proposed pattern is to replace the Ordinary Level papers at the end of the fifth-form year by new papers in the second sixth-form year as the university test of a candidate's general education, although it is assumed that most boys and girls will continue to take and to pass the same range of Ordinary Level subjects as they now commonly do before entering the sixth form. Under it the entrance requirements would be in two parts, a general and a course requirement, each of which must be fulfilled. The latter would be confined to passes in the General Certificate of Education examination, and including at least two Advanced Level passes. The General requirement would consist of required passes in the following new papers, taken not earlier than January in the candidate's second year in the sixth form: a paper in the use of English; a general paper; and a paper in the use of foreign language. The first would be designed to encourage the serious study of the use of English in the sixth form; the second should be set on the assumption that at an earlier stage candidates will have passed at Ordinary Level in either mathematics or a science subject and also in two or three of the usual arts subjects.

The proposals leave room for variation between universities both in the general requirement and in course requirements, and if the new pattern is adopted a transitional period will be necessary during which universities will allow candidates to fulfil requirements either of the existing pattern or the new. The timing suggested for the examination for this new general requirement, however, would reinforce the efforts already being made by the Secondary School Examinations Council and other bodies to reduce the excessive weight of Advanced Level syllabuses. Moreover, through the firm claim established on a reasonable proportion of sixth-form time for general studies it should afford a wholesome check to excessive specialization and influence those who prescribe syllabuses and the examiners who deploy them to do so in a realistic manner.

The note of sanity and realism in these proposals should be widely welcomed in the world of science. While they will do nothing to reduce the competition for university places, they should offer a fair prospect of checking premature specialization than earlier measures that have been tried in individual universities, and, particularly by fostering the study of English in the sixth form, assist to remove one weak-

* Committee of Vice-Chancellors and Principals of the Universities of the United Kingdom. Report of a Sub-Committee on University Entrance Requirements in England and Wales. Pp. 23. (London: Association of Universities of the British Commonwealth, 1962.) 2s. 6d.

ness in the scientist and technologist that has been a wide source of complaint and criticism. The fact that most universities are already known to agree with the proposals is promising, but it is to be hoped that those who have expressed opposition in principle will not fail to come into line. Simultaneously, with the re-examination of syllabus in the science subjects themselves, it offers an opportunity of improvement that is unlikely to recur but which if seized with vision and determination could transform the whole training of the science graduate. Any university should hesitate before raising obstacles or imposing requirements which could cause the opportunity to be missed.

THE MELLON INSTITUTE

THE annual report of the Mellon Institute for the year ended February 28, 1962*, records expenditure of 5·9 million dollars on independent and sponsored research. At the end of the year the Institute's staff was 561, and 362 professional and technical members were reporting on some 100 investigations. A list of publications of members during 1961 other than patents or periodicals or reports that do not appear in the open literature is included. Eighteen appointments at the level of Fellow were made during the year, half of whom joined Independent and half Sponsored Research. The Research Services of the Institute in its Instruments Section placed emphasis on systems which completely programme experimental procedures and increase the amount and accuracy of the information recorded. An instrument was constructed for the automatic recording of additives during redox measurements, a low-temperature (40° K to ambient) controller designed and built for the magnetic susceptibility programme and a circuit design of the instrument and servo system completed for a 'hot hardness tester'. In the Physicochemical Section the study of adsorbed organic molecules on catalysis by infra-red spectroscopy was extended, and a study initiated to find a correlation, if any, between the presence of trace elements and the occurrence of cataracts of the eye. The Microbiology and Microscopy Section completed a study of microbiological sludge inhibitors for jet fuels.

Under independent research, the report records continuing work on the detailed characteristics and distribution of plasma and red-cell hydrolytic enzymes, with special emphasis on the enzymes of the circulating blood which attack the hypotensive polypeptides, bradykinin and kallidin. Investigations are being continued on the interrelation between metabolites of *p*-aminobenzoic acid and aniline hydroxylation by resting cells of acid-fast bacteria, and completion of an electron microscopical study of ribonucleic acid from tobacco mosaic virus is reported. In organic chemistry, besides investigations of the acylamidines, the rotational isomerism in mono- and di-alkylpropenes of the types $R.CH_2.CH=CH_2$ and $R_2CH.CH=CH_2$ has been investigated by nuclear magnetic resonance spectroscopy, and a five-step synthesis developed of 1 : 2 : 3-triphenyl-4 : 5-benzpentalene. Efforts are being directed to develop general routes for the synthesis of branched polymers of the star type and of the comb type, and the stereochemical structures of polymers prepared by free-radical polymerization of methyl methacrylate have been computed from high-resolution nuclear magnetic resonance spectra measured at room temperature in chloroform solutions. Preliminary experiments have been made on the effects of heterogeneity in chain length, in chain branching, and of diluent on the relation between molecular weight and flow of high polymers in bulk or in concentrated solution. The basic studies in co-ordination chemistry led to the discovery of several unusual complex compounds, including a univalent iridium compound which reacts at normal conditions with a number of molecules commonly regarded as relatively inert. In physical chemistry, low-frequency infra-red spectroscopy and the vibrational spectra of inorganic substances have been particularly fruitful fields, and in radiation chemistry the electron-spin-resonance studies of radicals have been extended to a variety of hydrocarbons. Photochemical investigations largely focused on such systems as phosgene–olefine mixtures, 1 : 2-dichloroethylene and ethyl and vinyl iodides. Work continued on a mathematical theory of fluid behaviour within which many fluid–flow problems can be solved, and attempts are being made to find exact solutions for the steady-state Schrödinger equation for systems of two or more electrons in the potential field existing in an arbitrary molecular framework.

In metal physics, low-temperature calorimetry studies are in progress to obtain more reliable data for the copper–zinc and related binary systems. The study of stacking-fault probabilities in noble metal alloys has been extended to the silver–cadmium system, where a linear relation between the faulting probability and composition has been observed over compositions containing 0–30 atomic percentage of cadmium.

A group of investigations concerned with public welfare range from air purification, the processes involved in the deterioration of artists' materials, toxicity of new organic chemicals, industrial hygiene, mine acid control, steel protection and water resources. Notes are also included on progress in projects concerned with the development of solid catalysts from bone products for organic reactions; ceramic chemicals; aspects of forming and treating structural clay products and performance of plant scale equipment; starch-based chemicals as textile warp sizes; the performance of industrial fabrics from felt; ferrous alloys; a hydrogenation method for determining low concentrations of organic sulphur in natural gas; the chemistry of petroleum genesis; the fundamental nature of the activity of catalysts; studies of metal surfaces in hydrogenation; silicones; the synthesis of phosphonitriles; and the degree of susceptibility of selected high-strength case steels for rocket motors and other alloys to stress-corrosion cracking.

* Mellon Institute. Annual Report, 1961. Pp. 36. (Pittsburgh, Pa.: Mellon Institute, 1962.)