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THE THOMAS GRAHAM LECTURE 1991 *

'Thomas Graham—Would his Research be α-Unfunded Today?'

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1 Introduction

Thomas Graham (1805—1869) was head of the Department of Chemistry at University College London from 1837 to 1855 and Master of the Mint from 1855 to 1869. One of his biographers said of him [1]

> 'If, along the highroad of Chemistry, temples were erected to the memory of masterminds who moulded and guided the science forward into the unknown future, one of the greatest of these would be to the memory of Thomas Graham.'

These are strong words, and perhaps need some justification, as does the existence of a Royal Society of Chemistry Lecture named in his honour. The stated purpose of this biennial lecture series is 'to give distinguished Chemists, who are also active in public affairs, an occasion on which to express their views on broad, significant issues'. Thus previous lectures have been concerned with science policy, science and technology, biotechnology, scientific conscience, environmental research and development, and issues of defence.[2] In this year's lecture, however, I thought it appropriate to devote part of the lecture to Thomas Graham himself. The reason for this was in part because the second established chair of Chemistry in this Department now carries his name but also, and more importantly, because he was one of the founders and the first president of the Chemical Society in 1841, the 150th anniversary of which was celebrated only a month ago. Apart from the distinguished science and public service which marked his career, Graham was also responsible for pioneering the teaching of Chemistry in the U.K. *via* the mechanism of personal experiment by the student.

*Delivered at University College London on Thursday 9th May 1991.

[1] 'University College London' 1826—1926, by H. H. Bellot, University of London Press, 1929, pp. 127 and 286, quoting J. N. Collie.

[2] 1979 Sir Geoffrey Allen, F.R.S., Chairman, Science Research Council, 'Do We really have a Policy for Science?'; 1981 Sir Ronald Mason, K.C.B., F.R.S., Chief Scientific Advisor, Ministry of Defence, 'The Politics of Science and Technology'; 1983 Dr. R. F. Coleman, Director, Laboratory of the Government Chemist, 'Biotechnology—The Need for Collaboration between Industry, Academe and Government'; 1985 Professor Meredith Thring, Queen Mary College, London, 'The Conscience of the Applied Scientist'; 1987 Sir Hugh Fish, C.B.E., National Environmental Research Council, 'Chemistry in Environmental Research and Development'; 1989 Sir Richard Norman K.B.E., F.R.S., Chief Scientific Advisor, Ministry of Defence, 'Research and Development in Defence'.

In this respect he sought to follow the German tradition, in particular that of Liebig in Giessen

Graham's interests lay across the borderline between what we now call inorganic and physical chemistry, as indeed do mine I started my research life by studying diffusion-controlled reactions, for Graham, however, diffusion was the guiding thread, the abiding interest, that led him through the majority of his research—on gases, on liquids, on solids in liquids, and on gases in solids

I have divided this, the seventh Thomas Graham lecture, into four parts first, a biographical survey of the life and accomplishments of the man, second, a more detailed assessment of his principal contributions to scientific knowledge, third, a survey of other major happenings within the University of London, the U K , and abroad in which Graham might have played a part, and fourth, an assessment of the crisis in the funding of University Chemistry today

2 Survey of Graham's Life[3–9]

A. Early Life.—Thomas Graham was born on 21 December 1805 in Glasgow and entered the University of Glasgow in 1819 with the view to becoming a minister in the established church of Scotland At University he rapidly became influenced by Professor Thomas Thomson (Chemistry) and Dr William Meikleham (Natural Philosophy) He graduated as M A in 1824 and then studied for a further two years at Glasgow, supposedly in Divinity However it is clear that in reality he continued, in part at least, to study both Chemistry and Natural Philosophy His father, a successful merchant and manufacturer, was insistent that his son should continue with his studies of Divinity whereas Thomas Graham was, by 1826, equally determined that he should not By an elaborate ruse (and with the covert acquiescence of both his mother and sister) he managed to persuade his father that Divinity was taught better in Edinburgh than in Glasgow,[8] and so he moved there with the approval of his father in 1826 Records clearly show, however, that it was the Medicine and not the Divinity course for which he was registered, and that he was thereby able to continue his studies of Chemistry with Drs Thomas Hope and George Longstaff He also became acquainted with Dr Edward Turner in the Edinburgh department, and some fascinating correspondence survives on his views of Turner who, in 1828, was an applicant for the Foundation Chair of Chemistry at London University (which we now know as U C L) It is clear that, although Graham did not have a particularly high opinion of Turner as a scientist, he was nevertheless anxious that Turner should get this position in order that Turner's in Edinburgh might in

[3] Dictionary of Scientists p 493 Dictionary of National Biography 1890 **22** 361

[4] Thomas Graham in Essays in Historical Chemistry ed E Thorpe Macmillan London 1923 p 206

[5] R A Smith *Proc Roy Soc* 1870 **18** 17

[6] W Odling in Great Chemists ed E Farber Interscience New York 1961 p 553

[7] The Making of a Chemist Thomas Graham in Scotland by M Stanley Lochee Publications Ltd 1987 p 1

[8] The Department of Pure and Applied Chemistry A History 1830 1980 by R H Nuthall University of Strathclyde 1980

[9] M Stanley *Chem Brit* 1991 239

turn become available to him. In fact this did happen, and Graham taught Turner's classes in Edinburgh in 1828.

Graham was elected to the Fellowship of the Royal Society of Edinburgh in 1828. Shortly thereafter, however, his father, having grown anxious at the lack of reports of any preaching by his son—decided to visit him there. He found the lodgings full of scientific books and apparatus and no evidence whatsoever of any devotion to studies of Divinity. Graham's father proceeded to destroy the apparatus and to ban his son from entering the family home again! It was some years before they became reconciled.

In 1829, Graham was appointed Lecturer in Chemistry at the Mechanics' Institute in Glasgow and, in the following year, Professor of Chemistry at Anderson's College (now the University of Strathclyde). This was an important appointment, since it gave him the scientific base from which to develop his early research work. Despite the fact that he was not thought to be a particularly good lecturer, Graham increased the number of students of Chemistry (mostly, of course, medical students) from 61 in 1831 to 180 in 1834—6.

B. Significant Early Work.—Graham's first paper in the *Annals of Philosophy* in 1826 was on 'Absorption of Gases by Liquids', and his first paper on gaseous diffusion appeared in 1829. However, his first important paper was read to the Royal Society of Edinburgh in 1831—'On the Law of the Diffusion of Gases'—in which he established experimentally that the rate of diffusion of a gas is proportional to the reciprocal of the square root of its density. There followed a series of other equally important papers on quite unrelated topics:

1833 The Royal Society: 'Research on the Arseniates, Phosphates, and Modifications of Phosphoric Acid.' In this paper he established two new and wholly unanticipated classes of compound—polybasic acids and salts of anhydro acids.

1835 The Royal Society of Edinburgh: 'On Water as a Constituent of Salts'.

1836 The Royal Society: 'Enquiries respecting the Constitution of Salts'—for which he was awarded the Royal Medal.

Graham was elected a Fellow of the Royal Society on 15 December 1836, his nominators being E. Turner, M. Faraday, R. Phillips, J. F. Daniell, J. Dalton, and W. Henry. In the period 1837—1841 Graham produced his textbook *The Elements of Chemistry* which contains, according to his biographer, William Odling,

> '... one of the most masterly statements of the first principles of Chemistry that has ever been placed before the English Student.'

The book ran to three further editions, plus one American and one German edition.

When the chair of Chemistry at U.C.L. again became vacant, in 1837, Graham was very keen to be appointed to it. His anxiety on the matter is evident in a number of letters to his mother and sister One of the letters, dated 29 April 1837, displays considerable concern at the dominant role played by the medical fraternity in the appointment

> 'In whatever way it goes, the appointment will be made by medical professors, who will take care to be unanimous, or nearly so'

Graham had powerful backers and strong references as witnessed by the testimonial by Thomas Thomson

> 'If genius, industry and knowledge enter into the views of the electors to the vacant chair of Chemistry at University College, I am aware of no person who has a better claim than Mr Graham'

Graham was indeed appointed, his letter of acceptance being dated 21 June 1837 In that year Chemistry was taught in the Department to a class of 221 students, the largest such group in the U K U C L has recently acquired a painting of Graham of around this period

Graham took an active part in the founding of the Chemical Society in 1841 and was chosen to be its first President [10] He was by this time—and certainly with the death of Dalton in 1844 and the shift of Faraday's research more towards Physics—acknowledged to be the leading British chemist of the day and a worthy successor to Black, Priestley, Cavendish, Wollaston, Davy, and Dalton

The other important papers of Graham to appear in the next few years were

1846—1849 The Royal Society papers published 'On the Motion of Gases'—awarded a second Royal Medal in 1850 These papers were really to do with the law of effusion of gases
1850 Royal Society 'On the Diffusion of Liquids'—Bakerian lecture of 1850
1854 Royal Society 'On Osmotic Force'—Bakerian lecture of 1854

During this period Graham also played an important role as member of various external committees and commissions, *viz*

1846 Member, Commission reporting to House of Commons on the ventilation of the new Houses of Parliament
1847 Member, Board of Ordnance inquiring into the various methods of casting guns
1851 Member, Committee reporting on purity of water supplied by companies to the metropolis
1851 Vice-President, jury on chemical and pharmaceutical products at the Exhibition of 1851

[10] The Chemical Society 1841 1941 by T S Moore and J C Philip The Chemical Society London 1947 The Jubilee of the Chemical Society of London Harrison London 1896

He also acted for several years as one of the non-resident assayers for the Mint. This proved to be of critical importance since the next important step in his career was to the Mastership of the Mint in 1855.

It is difficult to understand the real motives of Graham in seeking this appointment but they were probably to do with the salary or the perceived power attaching to the position of Master of the Mint. It is intriguing to learn that the position had been taken away from the politicians in 1850 in favour of 'outsiders', with a concomitant reduced salary of £1500 p.a. (the salary for a professor at that time was about £500 p.a.).[1] The first such appointee was the Astronomer Sir William Herschel.

The Mastership proved to be a difficult position, making heavy demands on time devoted to the reorganization of the Mint. In consequence, Graham was unable to publish any further original scientific work until 1861 but, in subsequent years, three important papers were published. They were:

1862 'On Liquid Diffusion applied to Analysis', for which Graham was awarded the senior medal of the Royal Society, the Copley Medal for 1862.
1863 'On the Molecular Mobility of Gases'.
1866 'On the Absorption and Dialytic Separation of Gases by Colloid Septa'.

Clearly, Graham's work was regarded as being of the highest quality; indeed, it is described by his biographer William Odling as

> '... essentially that of detail, original in concept, simple in execution, laborious by its quantity, and brilliant in the marvellous results to which it led.'

Graham was invited to allow his name to be proposed for President of the Royal Society but he declined, partly on grounds of ill health and partly in fear that this office would interfere with that of Master of the Mint.

3 The Key Scientific Contributions of Thomas Graham

A. Graham's Law.—It was Thomas Graham[10,11] who had the genius to recognize the major physical phenomena underlying the motion of gases. There are, in the absence of conditions giving rise to turbulent flow, three main types of isothermal gas transport through tubes or porous media.[12–15] These are what we today distinguish as:[14]

(i) '*Effusion*, now more commonly called free-molecule or Knudsen flow. Here the *pressure is so low that collisions between molecules are negligible* compared with collisions of molecules with the walls of the tube or porous medium.
(ii) *Transpiration*, or laminar viscous flow, in which the gas acts as an isotropic continuous fluid driven by a *pressure gradient*. This is sometimes called

[11] T. Graham, *Philos. Trans. R. Soc. London*, 1846, **4**, 573; T. Graham, *Philos. Mag.*, 1833, **2**, 175, 269, 351.

convective or bulk flow. Here the pressure is high enough so that molecule–molecule collisions dominate over molecule–wall collisions.
(iii) *Diffusion*, the spontaneous intermixture of gases in contact, in which the different species of a mixture move under the influence of *composition* gradients. This is still a 'continuum' phenomenon in the sense that molecule–molecule collisions dominate over molecule–wall collisions.

There are other types of gas transport, such as thermal diffusion in a temperature gradient, surface diffusion of adsorbed molecules, and thermal transpiration. In addition, of course, the three main types of gas transport may occur in combination; in particular, flow and diffusion usually occur together.

The distinction between viscous (bulk flow) and diffusive transport holds only in the continuum regime; in the free molecule regime the molecules act independently.

Graham's law of *effusion*, sent to the Royal Society in 1846, states that the rate at which different gases at low pressure pass through small holes in a thin plate into a vacuum depends on the inverse of the square root of the density.[11] On the basis of the kinetic theory of gases (developed over a decade later) the view is that the number of molecules escaping in a given time through an orifice into a vacuum is equal to the number, in their random motion, which happen to hit the orifice; that is, they escape individually and randomly and, in the ideal circumstance, every molecule which enters the orifice escapes. The number of molecules hitting an orifice is proportional to the average molecular speed, $\bar{c}$; since the molecular kinetic energy of different gases at the same temperature and pressure is the same, it follows that $\bar{c}$ is proportional to $1/M^{\frac{1}{2}}$, where M is the molar mass. A modern statement of Graham's law of effusion is that the molecular flux (number of molecules crossing unit area in unit time) is proportional to $\bar{c}$ and thus to $1/M^{\frac{1}{2}}$, or that

$$\frac{J_1}{J_2} = \frac{\bar{c}_1}{c_2} = \left(\frac{M_2}{M_1}\right)^{\frac{1}{2}}$$

The curiosity is that Graham's law of *diffusion* (dating originally from 1831, some

[12] E A Mason and B Kronstadt, *J Chem Educ* , 1967, **44**, 740
[13] A D Kirk, *J Chem Educ* , 1967, **44**, 745
[14] E A Mason and R B Evans, *J Chem Educ* , 1969, **46**, 358 The argument that the diffusive flux (J_{iD}) of gas i, mass m_i, mean molecular speed $\bar{c}_i$, is proportional to its momentum ($m_i\bar{c}$) is as follows Take the average diffusion velocity for gas i to be V_{iD} (~ 1 cm s^{-1}), then $n_iV_{iD} = J_{iD}$, where n_i is the molecular density Since the momentum transferred by the ith gas in unit time to the walls of the container is equal to the mean momentum transferred per molecular impact (proportional to m_iV_{iD}) multiplied by the number of molecular impacts per unit time (proportional to $n_i\bar{c}_i$), the momentum transfer to an intervening membrane is (m_iV_{iD}) ($n_i\bar{c}_i$), which equals $J_{iD}m_i\bar{c}_i$ In the absence of a pressure gradient on a porous membrane separating two gases 1 and 2, it follows that $J_{1D}m_1\bar{c}_1 = J_{2D}m_2\bar{c}_2$ Thus $J_{iD} \propto (m_i\bar{c}_i)^{-1}$, and

$$\frac{J_{1D}}{J_{2D}} = \frac{m_2\bar{c}_2}{m_1\bar{c}_1} = \left(\frac{m_2}{m_1}\right)\left(\frac{m_1}{m_2}\right)^{\frac{1}{2}} = \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}}$$

[15] R B Evans, L D Love, and E A Mason, *J Chem Educ* , 1969, **46**, 423

15 years earlier) has the same functional form. This law relates to a constant pressure experiment, in which gas mixing is driven by a concentration rather than a pressure gradient.[11] The simplest physical explanation is based on a calculation of the momentum transferred to the walls of a porous membrane between two gases. Since there is no force on the membrane if there is no pressure differential, it follows that the momentum transferred to the membrane by one of the diffusing gases is exactly balanced by an equal and opposite momentum transferred by the other. If this argument is pursued it follows that, because the diffusive flux, J_{iD}, of gas i is inversely proportional to its momentum,[14] the same equation holds in these circumstances as well. Thus:

$$\frac{J_1}{J_2} = \frac{M_2\bar{c}_2}{M_1\bar{c}_1} = \left(\frac{M_2}{M_1}\right)\left(\frac{M_1}{M_2}\right)^{\frac{1}{2}} = \left(\frac{M_2}{M_1}\right)^{\frac{1}{2}}$$

The law of effusion is exact provided that the mean free path of the molecules is larger than the dimensions of the orifice. The range of validity of the law of diffusion is not restricted by geometric considerations but does have other restrictions to it.

The two phenomena, effusion and diffusion, are different from transpiration (viscous flow or equal flux diffusion) down a capillary, as indicated earlier. This third phenomenon was first investigated by Loschmidt, and involves the cross-section, S_{12}, for collision between molecules of the interdiffusing gases, 1 and 2. Transpiration thus depends on effective molecular diameters through S_{12}, from which the diffusion coefficient, D_{12}, may be obtained. It is therefore this process that is the subject of most modern experiments whose aim is the study of intermolecular forces. The well known 'smoke ring' experiment which probes the diffusion of ammonia and hydrogen chloride towards each other from opposite ends of an air-filled tube, is primarily concerned with transpiration.

Many experiments—including Graham's diffusion at uniform pressure through a frit of *ca.* 1 μm pore size—occur under conditions in which the gas can be described neither as a continuum fluid nor as a collection of completely independent molecules; instead, the gas behaves in the intermediate regime.

Graham suggested that effusive flow may be the basis for the separation of gases of different molecular mass, a suggestion which has proved to be of enormous importance. He coined the word atmolysis for the process of separation of gaseous mixtures by passage through rubber, clay, or metals.

B. Arsenates, Phosphates, and Modifications of Phosphoric Acid.—The second important contribution which Graham made was his discovery of the wholly new class of substance, the polybasic acid, *i.e.* the class of hydrated acid having more than one proportion of water replaceable by metallic oxide. He established the existence of ortho, pyro, and metaphosphoric acids and concluded that the properties of the acids required that each must contain chemically combined

[16] T Graham, *Philos. Trans. R. Soc London*, 1833, 253.

water[16] Graham's recognition that these acids are related through loss of water is significant, but it should be noted that he also demonstrated the analogous relationships among the three sodium salts His results in this area (presented in modern rather than Berzelius' nomenclature) are best illustrated by way of Scheme 1[16] Berzelius did not subscribe to Graham's views on this subject, claiming that the different species were all isomers of P_2O_5 He wrote

> Graham belonged to those who search for the spectacular and are easily deceived

But it was Berzelius who was, in fact, incorrect

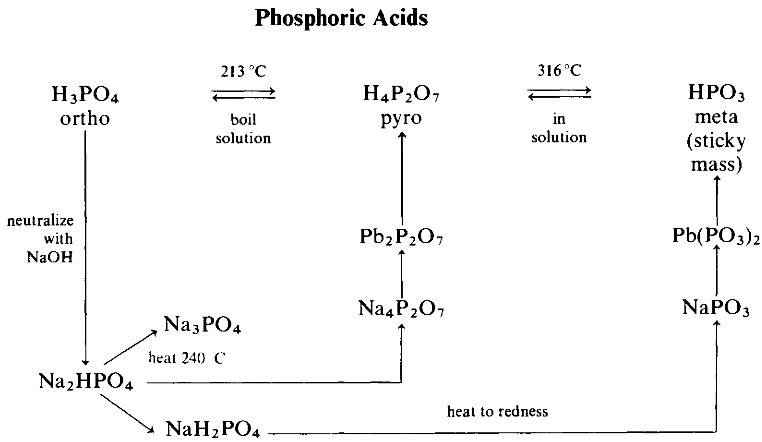
Graham also carried out a considerable body of research on water as a constituent of salts, in particular of vitriols and alums Thus he reported that for blue vitriol, $CuSO_4\ 5H_2O$, four molecules of water were expelled at 100 °C but the fifth at 240 °C (derivative thermogravimetric analysis now clearly indicates that in fact the first four molecules of water are each expelled at a different temperature between 70 and 130 °C, the exact temperatures being dependent on the heating rate) He reported similar behaviour for white vitriol, $ZnSO_4\ 7H_2O$ He also showed that the enthalpy of hydration associated with the first molecule of water is much larger than that associated with each of the subsequent molecules His research in this area clearly indicated differences in bonding of the different water molecules in these salts, and thus pointed the way to Werner in his eventual formulation of coordination chemistry Graham was also the first person to demonstrate that alums contain 24 molecules of water, *viz* $M^{I}_{2}(SO_4)\ M^{III}_{2}(SO_4)_3\ 24H_2O$ or, as we would now write the formula, $M^{I}M^{III}(SO_4)_2\ 12H_2O$

These few comments have had to be brief and can barely do justice to Graham's contributions to Inorganic Chemistry or to his thinking, as logical successor to Dalton, on the subject

C. Colloids.—The third major area to which Graham contributed was that of colloid chemistry Some colloids were known long before Graham's work, *e g* of gold, sulphur, prussian blue, *etc*, but it was Graham who first defined the field and who coined the word colloid itself (Gk glue-like) Graham introduced the term in 1861 to describe suspensions of one material in another, suspensions that did not separate on standing He recognized that colloids consist of a dispersed phase (now known to consist of particles of size 5 nm—0 2 μm) and a dispersive medium

Graham termed a mobile colloidal solution a sol, and one which has set to a semi-solid state a gel, he found that gels diffuse only very slowly through parchment membranes His early experiments were concerned with gelatin, albumin (M_r 17 500), rubber in benzene (M_r 6500) and silicic acid (M_r 49 000), experiments in which he recognized that the key character of colloids arises from their large surface/volume ratio

The area of Graham's research has since grown enormously, as may be seen by the wide range of disperse systems now known and continuously studied (Table 1)



Scheme 1 (Ref. 16)

Table 1 *Disperse systems*

Smokes and dusts: solid particles dispersed in gaseous media
Fog, mist, cloud, aerosols: liquids dispersed in gaseous media
Ruby glass: colloidal gold dispersed in glass
Suspension: solid dispersed in liquid
Emulsion: liquid dispersed in liquid
Coagulation (Graham used the term 'pectinization', from Greek: curdles): term for aggregation of a colloid such that it becomes a visible solid
Sol: colloid solution
Gel: a colloidal system which has set to a semi-solid state with supernatant liquid; it is the result of a partial or incomplete precipitation of a sol

Graham's work in this area led to the consideration of diffusion in liquids and thus to dialysis, the process of separation of species in solution by selective diffusion through a semi-permeable membrane. He showed that colloids could function as semi-permeable membranes. He also carried out many studies of osmosis, and an illustration of one of his osmometers is shown in Figure 1, along with other pieces of his apparatus.

4 The Mint, and Studies of the Occlusion of Hydrogen in Palladium

Graham brought about many reforms and economies at the Mint during the period 1855—1861. The chief of these was the withdrawal of copper coinage in favour of bronze (Cu 95%, Zn 4%, Sn 1%), which is much harder wearing. He became an increasingly important public figure, being consulted over affairs of state by the Chancellor of the Exchequer and Secretary of the Treasury. He was responsible for producing coinage not only for Britain but also for the Colonies. Moreover, he was an advocate—albeit an unsuccessful one—of metric weights and measures, of decimal coinage, and of international coinage. Despite all this,

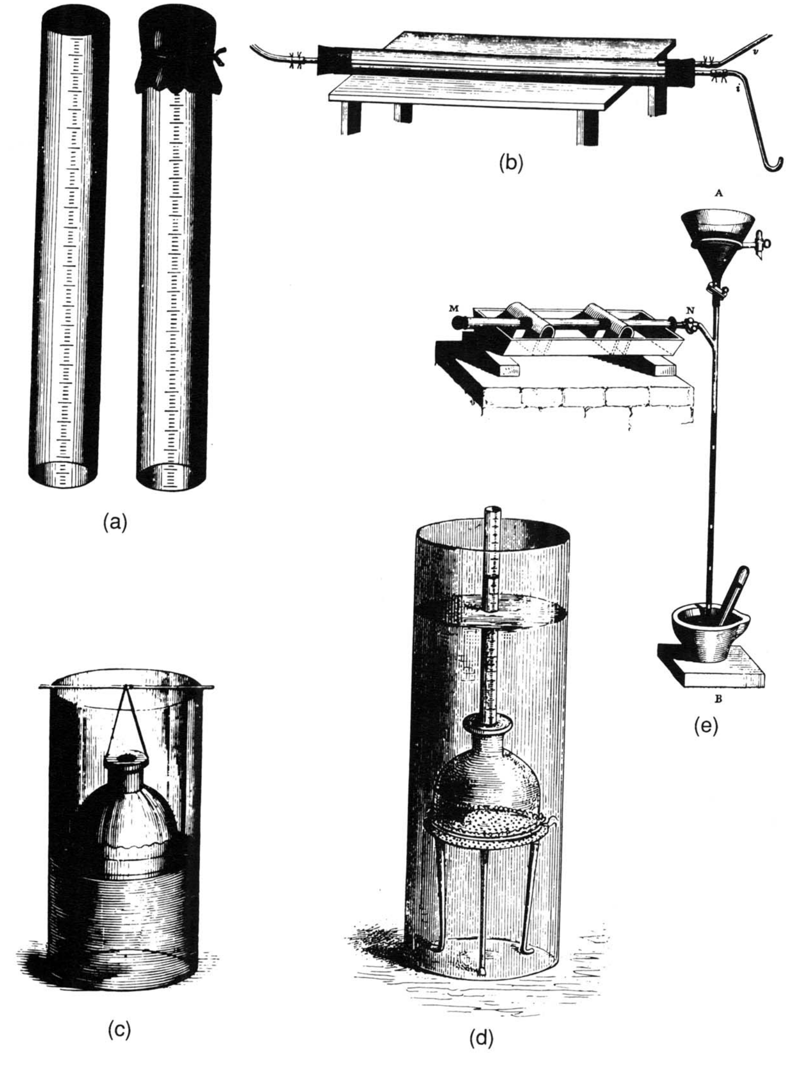


Figure 1 *A selection of Graham's equipment (a) diffusiometer (calibrated glass tube capped by a thin porous plate of compressed graphite) (b) atmolyser (porous earthenware tube through which a mixture of gases could be passed the more diffusive constituent being drawn into a vacuum jacket surrounding the tube) (c) bulb dialyser (d) osmometer (e) apparatus for investigating the occlusion of hydrogen into platinum metal heated inside a glazed porcelain tube and controlled by a Sprengel pump (Ref* 20)

Graham's general administration in his final years did cause some anxiety and, with his death in 1869, the title of Master of the Mint passed to the Chancellor of the Exchequer where it has remained ever since Whether the implied criticism was fully justified is, however, far from clear. Indeed, it is obvious that A. W. Hofmann had a different view of the matter since, in his obituary to the German Chemical Society in 1869, he said of Graham's period at the Mint:[6]

> 'The new chief of the Mint soon showed a vigilance, a knowledge of the work, and industry and energy and, when called for, unsparing severity on some officials of the establishment. Such controls had not previously been exercised. The new master's love of innovation and his disturbance of settled arrangements were resisted and it took Graham some years to overcome the difficulties.'

Research on the properties of metals and alloys was clearly within the remit of the Master of the Mint.[17,18] And so it was that in 1866 Graham discovered that palladium metal could occlude 600 times its own volume of hydrogen. He later discovered that it could, at room temperature and pressure, in fact absorb up to 1000 times its own volume of hydrogen. We now know that the hydrogen atoms in palladium occupy octahedral vacancies and that the structure of the hydride approaches that of sodium chloride. Indeed, fine palladium powder can be made to reach $PdH_{0.7}$, 70% of the octahedral sites being occupied randomly at normal temperatures and pressures. Graham discovered that electrochemical loading of palladium with the latter as cathode in a cell is particularly efficient, indeed we now know that the bulk material reaches virtually PdH at NTP although, curiously, it reaches only $PdD_{0.7}$ with deuterium. Such loading is more easily accomplished at low temperature, *e.g.* in methanol at $-70\,^{\circ}C$. The occlusion of hydrogen is accompanied by expansion of the solid by up to 5% in lattice dimension; the hydrogen can all be removed in vacuum at $100\,^{\circ}C$.

Graham realised that hydrogen would diffuse through palladium, though by the mechanism of atomization at one surface, passage of hydrogen atoms, and then recombination at the other surface. Many vacancies remain in the PdH structure, aiding diffusion. Indeed PdH (α and β forms) is regarded as a reservoir for free atomic hydrogen. Graham also realised that palladium was far more effective than platinum in its effectiveness at the occlusion of hydrogen, that osmium and iridium were ineffective, and that when palladium is exposed to coal gas only the hydrogen enters the metal.

Graham's research then developed to the study of the absorption of hydrogen by alloys of palladium with varying percentages of silver, with the conclusion that absorption remains effective provided that the atomic percentage of silver is $< 50\%$. In all of this work Graham was greatly assisted by George Matthey who made the alloys;[19] clearly we have here an early example of the kind of industrial gift/loan scheme applied to precious metals, one which was subsequently developed effectively by what is the now Johnson Matthey company. The

[17] The Mint. A History of the London Mint from AD 287 to 1948, by Sir John Craig, Cambridge University Press, 1953, pp. 317–329.
[18] Sir John Craig, *Notes and Records of the Royal Society*, 1961, **19**, 156.
[19] A History of Platinum and the Allied Metals, by D. McDonald and L. B. Hunt, Europa/Johnson Matthey, London, 1982, p. 266.

modern outcome of Graham's research in this area is the design and operation of industrial equipment to generate hydrogen of high purity from a variety of intake gases Hydrogen generators now incorporate diffusion tubes made of silver–palladium alloy, the pure gas is used for the hydrogenation of edible oils, the manufacture of semiconductors, the annealing of steel, and the cooling of power station alternators

In his last paper to the *Proceedings of the Royal Society*, published only a few months before his death in 1869, Graham was actively advocating the view that hydrogen is the vapour of a highly volatile metal which he named hydrogenium, and thus that the Pd/H system is really an alloy To emphasize his views, he had struck at the Mint a number of palladium–hydrogenium medals (diameter *ca* 2 cm) which he proceeded to distribute to friends and associates [19] One of these was given to Sir William Herschel, his predecessor as Master of the Mint, and this medal has now been bequeathed to the Science Museum in South Kensington Another was given to the then Chemical Society and this medal is also held, though on loan, by the Science Museum and exhibited together with a number of other items (diffusiometers, osmometer, *etc*) The complete collected works of Thomas Graham were published in a single volume in 1876 [20]

5 Some Major Developments in the University of London, the U.K. and the Commonwealth in the 19th Century

In making a proper assessment of the influence of Graham on the scientific community at the time it is important to consider the major developments taking place in the University of London in the latter half of the nineteenth century in which he might have played a part Leading amongst these developments must have been the role of the University in providing examinations at other newly established Colleges [21] Those institutions indicated in Table 2 had to submit themselves to the University of London for examination and had neither University status nor authority to confer degrees until the 20th century (except

Table 2 *Foundation dates of 19th century U K universities examined originally by the University of London*

England	*Wales*	*N Ireland*	*Scotland*
Manchester 1851	Aberystwyth 1872	Belfast 1845	Dundee 1881
Leeds 1874	Cardiff 1883		
Bristol 1876	Bangor 1884		
Birmingham 1880			
Nottingham 1881			
Liverpool 1882			
Sheffield 1897			

[20] 'Chemical and Physical Researches by Thomas Graham collected by R A Smith Edinburgh University Press, Edinburgh, 1876

[21] 'The University of London and the World of Learning 1836—1986', ed F M L Thompson, Hambledon, London, 1990, p xxi, 'The University of London 1836—1936', by N Harte Athlone, London, 1986 p 96

Table 3 *Foundation dates of some 19th century commonwealth universities examined originally by the University of London*

Australia	*India*	*New Zealand*
Sydney (1850)	Bombay (1857)	Otago (1869)
Melbourne (1853)	Calcutta (1857)	Canterbury (1873)
Adelaide (1874)	Madras (1857)	Auckland (1882)
		Wellington (1897)

for Manchester from 1880 and the University of Wales from 1893). But the control exercised by the University was not confined to the U.K.; in 1850 the University obtained a supplementary charter which enabled institutions throughout the British Empire to be recognized for the purpose of permitting candidates to offer themselves for London degrees.[21] In this way the students of many Universities established in the 19th century (Table 3), and many more in the 20th century (both in the U.K. and abroad), were likewise originally examined by the University of London. It is clear that these Universities were not established in time to send research students to U.C.L. to work with Graham; the spadework in this respect was laid by his successor as Head of Chemistry at U.C.L., A. W. Williamson, and then developed by William Ramsay.

The first Australasian Chemists to come to U.C.L. to study for a Ph.D., in each case with William Ramsay, were Bertram D. Steele, B.Sc. (Melbourne), 1899 and Matthew A. Hunter, B.Sc. (1st), M.A. (Auckland), 1902. Steele went on to become Foundation Professor at the University of Queensland and to carry out significant research on arsenic-based herbicides. Hunter became the first person to isolate pure titanium metal (99.9%)[22] (at General Electric, Schenectady) and went on to become President of Rensselaer Polytechnic. Following on from these early connections, many other Australasians have studied at U.C.L.[23] and 15 Australians (N. T. M. Wilsmore, J. I. O. Masson, H. G. Poole, A. Maccoll, A. T. Austin, R. S. Nyholm, D. P. Craig, B. N. Figgis, T. M. Dunn, R. Bramley, R. A. Ross, B. Bosnich, T. M. Cresp, M. B. Ewing, and S. P. Best) and four New Zealanders (P. B. de la Mare, R. J. H. Clark, M. L. McGlashan, and D. E. Williams) have been at one time or another members of the academic staff of the Department.

The U.C.L. records are not sufficiently detailed to indicate whether any of Graham's students went to the Commonwealth to hold Chairs in any of their various Universities or University Colleges. The only London graduate to do so at around that time of whom I am aware was A. W. Bickerton[24,25] who was taught by Frankland (Chemistry), Tyndall (Physics), and Huxley (Biology) at the Royal School of Mines before accepting the Foundation Chair at Canterbury in 1873. Clearly Bickerton, primarily a teacher, albeit a very good one, who could

[22] M. A. Hunter, *J. Am. Chem. Soc.*, 1910, **32**, 330.
[23] A. Maccoll, *Ambix*, 1989, **36**, 82.
[24] 'The First Eighty Years', by H. N. Parton, University of Canterbury, Christchurch N.Z., 1985.
[25] 'A History of the University of Canterbury 1873—1973', by W. J. Gardner, E. T. Beardsley, and T. E. Carter, Caxton, Christchurch, N.Z., 1973.

count many distinguished people—including Ernest Rutherford—among his graduates, had hoped for much in Christchurch; his biographer said of him that he

> 'dreamed of an educationalist's heaven where professors and lecturers, free from all trammels of lay authority, and unrestricted by financial limits, enlightened their pupils on subjects which they considered essential and by methods which they had proved to be most efficacious'

An educationalist's heaven, however, was not to be found under the Southern Cross, and neither (as we shall see) is it necessarily to be found under the Pole Star.

Graham played no obvious part in setting up, advising, or examining the (then) colonial universities, being too early to be involved with the wider development of London University's influence overseas. But he contributed to the 1857/58 discussions on new Science degrees, with Frankland, Grove, and others supporting a wider rather than a more specialized syllabus.[26] It is impossible for him not to have been well aware of Australia and New Zealand in particular, owing to the three voyages of James Cook (1769, 1773, and 1776), the first of which had as its prime objective the scientific one of observing the transit of Venus across the sun on 3 June 1769 (of critical importance to navigation). Moreover, Cook's botanist on the first voyage, Joseph Banks, was to become a very important figure on the British scientific scene, becoming President of the Royal Society a position which he held for 41 years until his death in 1820.[27] This was only 16 years before Graham was elected a Fellow and it is thus not possible for him to have been unaware of Banks' many discoveries in Australasia and their consequences.

Graham's most direct link with antipodean development was in the training in assaying and in the support he gave to his student W. S. Jevons as assayer to the new mint at Sydney from 1854. Jevons returned to U.C.L. in 1859, and turned to political economy, first at Manchester then from 1876 again at U.C.L.[28] It is also unclear as to whether or not Graham approved of the establishment of the Royal College of Science in 1845 or of the Royal School of Mines in 1851. It is possible that he approved in fact since there is no evidence that he wished further to expand the Chemistry Department at U.C.L. at the time. In 1849 he had met A. W. Williamson and had supported his election as Professor of Analytical and Practical Chemistry at U.C.L.; Williamson was thus there ready to succeed him in 1855.

6 The Funding of Basic Research—the Crisis in Chemistry

There is no doubt that the funding of basic research in Chemistry in the U.K. is at a point of crisis. The budgets available have eroded to comparatively trivial

[26] D S L Cardwell, 'The Organisation of Science in England', Heinemann, London, 1972, p 94
[27] 'Joseph Banks', by P O'Brien, Collins Harvill, London, 1987
[28] R Konekamp, in 'Papers and Correspondence of William Stanley Jevons', ed R D Collison Black and R Konekamp, Macmillan, London, 1972

sums by the standards of those available to our major competitors in comparable departments in the West, particularly those in Germany, U.S.A., and Japan. The cost of front-line research in Chemistry, as in other scientific disciplines has, of course, escalated in recent years, largely through greatly enhanced powers of instrumental capability. These have generated detailed information that has wholly transformed our insights into Chemistry. By way of illustration, consider the infrared spectrum of SF_6 at 300 K in the $\nu_3(t_{1u})$ region at 948 cm^{-1} (Figure 2). The first reported spectrum, obtained in 1934 with a prism spectrometer, showed only a featureless absorption, as was true of many other spectra published over the next 30 years.[29] In 1969 the band was recorded at 0.07 cm^{-1} resolution, which represents about the best that most grating spectrometers can do; the PQR-branch contours and some additional Q-branches due to hot bands were resolved but no individual rotational lines. Within a year a tunable semi-conductor diode laser had been used to record positions of the band at Doppler-limited resolution (3×10^{-6} cm^{-1}); this revealed dense structure. At about the same time, sub-Doppler spectra saturation techniques were used to obtain spectra of small regions near to CO_2 laser lines, with a resolution of $< 10^{-6}$ cm^{-1}. To reveal full detail portions of this spectrum had to be recorded at an expanded scale such that it would have required some 50 miles of chart paper to cover the whole ν_3 band; indeed by 1977 some 10 000 vibration–rotation transitions had been observed in this one fundamental band and assigned. The new opportunities and challenges at the front line of research are clear (in this area, to the separation of uranium isotopes *via* the selective laser-induced decomposition of UF_6 molecules in the gas phase), but at a price. In a similar vein, temporal resolution of reactions could be probed some 50 years ago at (say) 1 s resolution whereas now, optical pulses of *ca.* 6 fs duration can be generated.[30] This has led to great developments in our abilities to measure spectroscopic processes as a function of time, and to peer into a world of events not previously accessible on a timescale shorter than that of a molecular vibration. A vast panoply of reactions has now become capable of study with the appropriate equipment, *e.g.* the transition state chemistry of the photochemical decomposition of ICN,[31] the excited-state *cis–trans* isomerization of bacteriohodopsin,[32] *etc.* There is no denying that it costs much money to operate at the front line of research; nevertheless, countless \$1 M laboratories are in operation in the US.A. and elsewhere, but very few in the U.K. The view in such countries is clearly not so much whether their scientists can afford to operate at the front line of research but whether they can afford *not* to! The funding in the U.K. of basic research in some areas is now at such a low level that the front line can barely be seen, let alone manned.

[29] R. S. McDowell in 'Advances in Infrared and Raman Spectroscopy', ed. R. J. H. Clark and R. E. Hester, Heyden, London, Vol. 5, 1978, p. 2.
[30] C. V. Shank, in 'Advances in Spectroscopy', ed. R. J. H. Clark and R. E. Hester, Wiley, Chichester, Vol. 18, 1989, p. 369.
[31] M. Dantus, M. J. Rosker, and A. H. Zewail, *J. Chem. Phys.*, 1987, **87**, 2395.
[32] R. Mathies, C. H. Brito Cruz, W. Polland, and C. V. Shank, *Science*, 1988, **240**, 777.

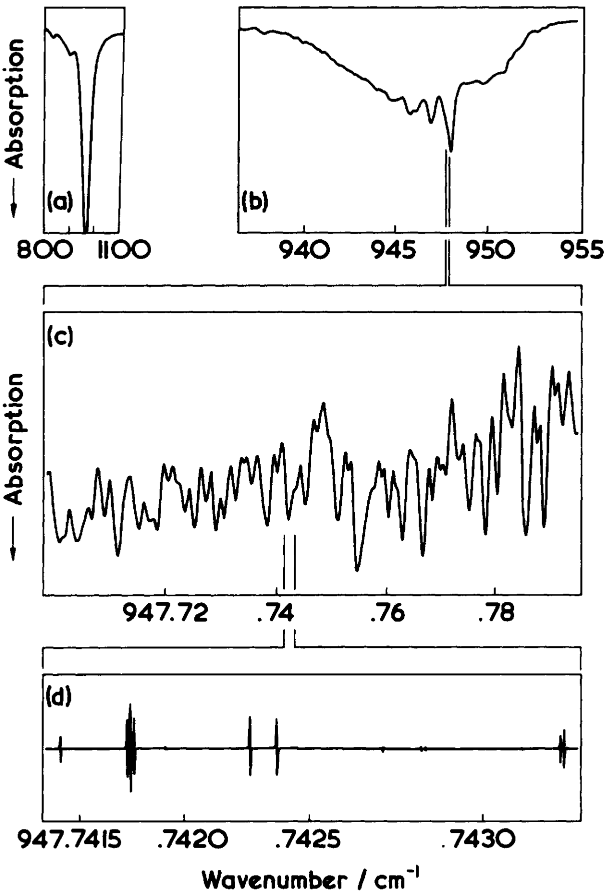


Figure 2 *The infrared-active band attributed to the* $\nu_3(t_{1u})$ *fundamental of* SF_6 *as it appears with increasing resolving power using* (*a*) *a* 1934 *prism spectrometer* (*b*) *a grating spectrometer* 0 07 cm^{-1} *resolution* (*c*) *a tunable semiconductor diode laser* 3×10^{-6} cm^{-1} *resolution and* (*d*) *a* CO_2 *laser* $< 10^{-6}$ cm^{-1} *resolution* (*Ref* 27)

E Bright Wilson asked some perceptive questions in 1986 on the matter of funding in his survey of one hundred years of physical chemistry [33] He asked

'Would the laser have been invented when it was, if all government agencies providing research funds had stuck closely to the role of supporting only mission-oriented research?'

'Would the laser have been brought forth by the National Institutes of Health offering project support for a new way of treating detached retinas? No!'

[33] E B Wilson *Am Sci* 1986 **74** 70

> 'The laser was developed because agencies were willing to support microwave spectroscopy as a pure science with no anticipation of the tremendous range of practical applications that would flow from the stimulated emission in ammonia.'

We have now seen countless of these developments in surgery, the printing of newspapers, spectroscopy, communication, geodesy, civil engineering, the laser guidance of missiles in warfare, *etc.* As with Graham's research, it is obvious that fundamental research in good hands pays off, it is simply the question of the time scale over which the investment may be recouped that is uncertain.

For those industrialists unfamiliar with the term 'α-unfunded' (the academics are *very* familiar with it) a word of explanation is needed. Over a decade ago when I sat on one of the relevant S.E.R.C. Committees, the members were required to place all proposals for research grants into one of three categories, α (top class research, essential that it be carried out), β (good research, worthy of being funded if there is sufficient money to do so), and γ (reject); the αs and βs were then graded individually. At that time all of the αs and about one-third of the βs were funded. Today, the funding situation is such that perhaps only one-quarter of the αs are funded. The remainder are referred to as 'α-unfunded'.

One serious question which we all must try to answer is 'why do we find ourselves in the situation of having so much potentially excellent research unfunded?' The answer seems to lie not in the first place with politicians but with the public, whose general appreciation of science is poor. We must, in this regard, accept the responsibility for not ensuring that our friends and relations are better informed of the benefits of research in science (in the first instance, a disinterested search for knowledge) whether those benefits lie in the field of pharmaceuticals, dyes, pigments, agrochemicals, plastics, semi-conductors, or whatever. Such topics should be capable of sustaining as good a dinner table conversation as any in law, sport, politics, the arts, *etc.*; yet we all known how difficult it is to carry out any sort of discussion in general company on scientific subjects. The public lack of appreciation of science shows in quiz programmes (*e.g.* Mastermind) in which the comparative triviality of the questions on science lies in stark contrast to sophisticated questions that are apparently acceptable in other subjects.

This matter was highlighted recently in an article in the *New Scientist* entitled 'Your Monet or your life', in which the writer drew attention to the large number of people who queued to see the exhibition of paintings by Monet (born 15 November 1840) (to which there is, of course, no objection) while doubtless blissfully unaware that they were doing so at the doors of the Royal Society of Chemistry (born 30 March 1841).[34]

> 'There you have the problem. Ordinary folk queuing to pay £5 per head to view impressionist paintings, and passing the door—without a glance—of an organization which helps to feed, clothe, protect, and heal them.'

It is unfortunately true that very few U.K. citizens, including the schoolteachers,

[34] J. Emsley, *New Sci.*, 15 November 1990.

Table 4

Student Numbers

U.K.	People	56 million
	Students	362 100
California	People	26 million
	Students	Research University 144 600 (University of California)
		State University 350 000
		Private University (Stanford, Caltec, *etc.*)?

The Times, Letter to the Editor, 31 October 1990

Gross National Product

% G.N.P. on research	U.K.	0.58%
	France	0.91%
	Germany	0.96%

The Times, Editorial, 1990

Research and Development

Total spending on R and D	U.K.	£9.7 billion
	France	£12.8 billion
	Germany	£19 billion

H. Atkinson, S.E.R.C. Report, quoted by the Science Editor, *The Times*, 1991

are aware of how effective the British Chemical Industry is in creating wealth for the nation. John Cox, Director of the Chemical Industries Association is quoted recently as saying that[34,35]

> 'The U.K. Chemical Industry produced goods to the value of £27 billion, with a profit of £3 billion, in 1989, and that this massive generation of wealth was made possible by only 322 000 workers.
> The Chemicals Industry is Britain's number one manufacturing exporter with a balance of payments surplus of £2 billion. The industry invests £2 billion p.a. in new plant.'

In student numbers ours in Britain compare unfavourably with those of California in particular and with those of the U.S.A., Germany, and elsewhere in general, as does the percentage of our G.N.P. going into research (Table 4). To improve these matters it is clear that we need much more effective publicity in the U.K. in order to improve the public awareness of Science. This should not simply be left to the Royal Society, the Royal Society of Chemistry, and other such bodies, it is something which we all must tackle as the individuals, since only in this way can any real pressure be put on our Government at the grass roots. The need for a scientifically literate and scientifically aware public is now urgent.

It is arguable that the best form of aid that could be given by the U.K. to foreign, especially third world, countries would be in the educational form, *i.e.* as grants to assist schooling in the countries concerned, and to assist in the training

[35] *The Times* 27 August 1990

of school teachers and of qualified scientists in the U.K. by way of bench fees, scholarships, *etc.* Emotively appealing as aid in the form of food *etc.* undoubtedly is, without the appropriate local educational infrastructure there can be no expectation that such problems will not recur indefinitely. Certainly at U.C.L. and elsewhere, countless applications are received from students in the third world, and now also in eastern bloc countries, wishing to study for either undergraduate or postgraduate degrees; almost none of these is it possible for us to support, much as we would dearly like to. What will happen to the new generation of Heyrovskys?[36] They will not be coming to the U.K. for their training in the absence of much more enlightened and generous governmental support than is evident in the TEMPUS scheme.

Thirty years ago Commonwealth scholars could apply to study for a higher degree in the U.K. in anticipation of receiving an I.C.I., Turner and Newall, Ramsay, 1851, or other such scholarship; these nurtured the seed-corn of a whole generation of university chemists. Today, the first two scholarships have long since ceased, while over the past two or three years the Ramsay Fellowship has had to be co-sponsored, either with Industry or with an 1851 Exhibition. In consequence, potential scholars from the Commonwealth—should they now even choose to go abroad at all for further studies—go predominantly to the U.S.A. to the mutual benefit of both parties. Accordingly I must appeal to those industrialists present to think much more positively than in the past about supporting basic research projects in Universities, and especially those in which the financial return may take rather more than 12 months to recoup! Moreover it is critically important to support schools and schoolteachers since, without the latter (and we see virtually no evidence of our graduates wishing to enter this profession, owing to its poor pay and conditions) there is little way in which our schoolchildren can be got interested in science in the first place. Whence, then, do we get our undergraduates and you, some years later, your new employees?

7 Conclusion

Graham's research was marked by the simplicity of his apparatus. Although it is difficult to know what the real costs of his experiments were in present-day terms, it is difficult to believe otherwise than that they were small; moreover in his last work, on the occlusion of hydrogen into palladium, the metal was either given to him or purchased *via* the Mint. How would Graham have operated had he been on the scene today? Would he have sought to set up an Interdisciplinary Research Centre (IRC) on Solid State Chemistry/Cold Fusion/Electrochemistry/21st Century Materials, subjects not far removed from those of the current Thomas Graham Professor at U.C.L.? Would his research have been α-unfunded unless he had called himself a Materials Scientist and applied for funding from the Materials Science and Engineering Commission (MSEC)? I think not. Though these are difficult questions to answer, my belief is that

[36] J. Heyrovsky, B.Sc. (1913), D.Sc. (1921) each from U.C.L. for work done with F G Donnan, Nobel Prize for Chemistry, Polarographic Institute, Prague, 1959.

Graham, as one of the great scientists of his day, would indeed have been funded and not been frustrated by the α-unfunded label I reach this conclusion more by an act of faith than anything else, and in the belief that the U K has sufficient sense to continue to fund curiosity-motivated research—albeit too little For it is significant that *all* of Graham's research—whether it be that on diffusion, polybasic acids, colloids, occlusion of gases in metals—was curiosity-motivated and not contract-motivated He would have held with the view that the primary aim of higher education is to stimulate and expand young minds by doing exploratory research at the limits of present knowledge rather than the view that only utilitarian research is worthwhile

A recent letter to *The Times* spells out the alternative [37]

> 'A country that has nobody working at the frontiers of research in a discipline will soon find itself with nobody who either understands what is happening at the frontier or what its implications are Third-world countries are not technologically backward because they haven't access to the published results of research, much more to blame is the lack of people who can understand it or make use of it Do we want to join them?'

The real question facing chemists in the U K today is not whether Thomas Graham's research would be α-unfunded, but whether Chemistry as a whole, on the Science and Engineering scene, might become α-unfunded That question, deep and disturbing, I leave with you to ponder

Acknowledgements I am grateful to Drs J H S Green and T Thiruna-machandran for assistance with some of the historical research

[37] Letter to *The Times* 18 February 1991