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Colloid Science: A Chapter in Chemistry.

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ONE of the minor exercises of one's youth consisted in taking a long country walk in company and on one's return writing down in essay form the impressive features of one's journey. One could not help being greatly impressed by the apparent diversity in the treatment of what was essentially the same subject matter. "Quot mentes tot sententiae." In the writing of that chapter of science which is now termed "colloid science," similar variations in emphasis will be imparted to it by different historians.

It is well known that our first President, Thomas Graham (1861), was responsible for the criterion of diffusibility as a distinction between colloids and crystalloids.

This recognition of the colloid state in its turn gave rise to a wide variety of preparative methods, both by condensation and by dispersion, since at that time the macromolecule as a colloidal entity had not been envisaged.

The foundations of the exact science, with its own particular discipline and methods, may be said to have been laid when recognition was given to the fact that separating any two bulk phase systems there always existed a third or interphase—Wolfgang Ostwald's "forgotten dimension." It is with the properties of what the late Sir William Hardy termed "matter in the boundary state" and with the effects of subdivision and dispersion which cause the interphase to become progressively more important in determining the behaviour of the system as a whole, that colloid science is concerned.

Liquid interfaces are surfaces of equipotential; since by their nature it is possible to determine the free surface energy by direct experimental methods and thus to test any theoretical relation it is not surprising that the thermodynamic treatment of liquid interphases was rapidly developed. The effects of curvature and charge on the equilibrium vapour pressure, and the composition of the surface phase of capillary active solutions, studied respectively by Lord Kelvin and Willard Gibbs, may be mentioned as two of the most important relations. It is of interest to observe how in the development of the science, important questions have been raised and regions of enquiry have been marked out in direct consequence of consideration of these two fundamental thermodynamic expressions.

Thus, the ascent of liquids in capillary tubes should in principle give us a method of determining the range of molecular action. In spite of the general acceptance of a force law of the type $\frac{A}{r^{12}} - \frac{B}{r^6}$ for non-ionic or apolar interaction, there is still discussion concerning the possible existence of long-range forces. Kelvin himself believed that capillaries of some 10μ diameter represented the lower limit at which the equation was applicable; but the recent work of Carman has made it clear that we can safely go down to molecular magnitudes, probably even down to one molecular diameter. The matter is clearly important in connection with the retention of vapours in liquid form in capillary systems such as charcoals, powders, or the multitudinous gel-like hydrated oxides.

Again, the ascent of liquids in capillary tubes may involve what is generally termed the wetting or contact angle. The equation derived from the simple application of the triangle of forces in the form

$$\cos \theta = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$$

where γ_{SV}, γ_{SL}, and γ_{LV} refer to the solid–vapour, solid–liquid, and liquid–vapour free energies, has been employed to gain some information on adhesion to solids and the effects both of surface roughness and of the nature of the solid surface examined.

It is in the correlation of thermodynamic with molecular concepts that problems arise. It is not difficult to visualise the concept of wetting or not wetting, but a finite wetting angle must involve specific molecular interaction. Water will wet clean mica in the sense that it will spread over the surface. If a monolayer of barium stearate is placed on the mica surface, a drop of water on this surface forms a re-entrant angle. If we now take a fresh mica sheet and treat it with a barium salt (*e.g.*, barium chloride) in order to replace the surface cations by barium and press this treated sheet on to the barium stearate covered surface, we find on cessation of the contact that the wetting angle on both mica sheets is now substantially the same and has a larger value than had the originally close-packed monolayer-covered sheet. Clearly we have transferred some of the stearate molecules from one sheet to the other, and the surface population of hydrophobic groups has thus a profound effect on the magnitude of the wetting angle and on the free-surface-energy changes involved in wetting.

The effects of relatively small changes in the surface population on the apparent free energy of the surface can be noted in quite a different field. It is well known that crystal growth can be modified by small additions of materials which are selectively adsorbed on certain facets of the growing crystal. Whilst the amount of, say, adsorbed cetylpyridinium bromide required to modify the growth of crystals of succinic acid is difficult to determine exactly, it is certainly less than a packed monolayer. If growth on the planes takes place at " Lockerstellen " or kinks in the molecular terraces it is possible that adsorption at these sites alone is necessary to control the growth.

The simplest application of the Kelvin equation to spherical drops has again in recent years been of importance in an understanding of the formation of mists and of aerosols. The free energy of a spherical drop of liquid can be written.

$$\Delta G = 4\pi r^2\gamma - \frac{4}{3}\pi r^3 \frac{\Delta}{M} \boldsymbol{R}T \log \frac{P}{P_0}$$

We see that, when $d\Delta G/dr = 0$, then $\boldsymbol{R}T \log P/P_0 = 2\gamma M/r_c\Delta$

thus the Kelvin equation gives us a means of determining the radius (r_c) of the smallest drop endowed with stability. Drops of smaller size are essentially unstable and are usually termed nuclei or embryos. During the process of condensation an embryo occasionally attains the critical size, whereafter it will continue to grow to form the mist. The work of Volmer and of Becker and Dorey is of special interest in this connection. The embryos for a number of liquids must acquire about 100 molecules before the critical size is attained; for solids, numbers as low as 7 molecules per embryo have been cited. It is evident that embryos formed from ionic constituents in which the " ordering" forces are great may attain a stable configuration and size more readily than those in which van der Waals forces alone are operative between the constituent molecules. It is clear that much has yet to be learnt about the mechanism of growth of the embryo.

We see that the Kelvin equation has given rise to a number of important considerations, many of which open up vistas of still uncharted territory.

In the same way the Gibbs equation and its implications may be said to be the thermodynamic background of a large section of the science. One of its most important consequences lay in the implication that the Gibbs dividing line could be placed one molecule below the free boundary surface, or that the Gibbs layer or the interphase was but one molecule in thickness. This led to the concept of the orientated monolayer, an idea advanced almost simultaneously by Devaux in France, Sir William Hardy in England, and Irving Langmuir in the United States. The properties of orientated monolayers of insoluble but film-forming materials have been the subject of much interesting work during the last thirty years.

We call to mind that such monolayers can exist in several states—gaseous, vaporous, liquid, and solid. The conditions of phase equilibrium, the free energies, the heat and entropy changes involved in two-dimensional phase transitions, as well as the identification of phase changes of second and higher orders, have all been separately investigated. Satisfactory equations of state for many of these two-dimensional systems have also been established both at liquid–liquid and at liquid–gas interphases. Every year we find additions to our knowledge of the surface pressures, potentials, and viscosities of such systems, and there is a continuous stream of records of the interesting results which arise from chemical reactions between similarly orientated molecules in the monolayer and reactants injected into the substrate.

It must also be observed that Gibbs never visualised the existence of different surface phases, the nature of which depends on the density of surface population. Whilst the assumption that the Gibbs dividing line can be drawn beneath the monolayer appears justified in many cases, it is certainly not valid for solutions of ampiphatic electrolytes at appreciable ionic concentrations. For such accumulations in a second and even in thicker layers appear to take place, apparently always above the " micelle " point. We still know little about the composition of the surface phase of binary mixtures. The progressive addition of soaps in emulsion systems reveals such interfacial accumulations in that the interface is reversed, first hydrophobic, then hydrophilic, and then hydrophobic again, whilst solvated orientated multilayers readily form on the surface of concentrated soap solutions.

More recently studies of the rates of attainment of surface equilibrium and of the rates of solution of the surface phase have revealed the existence of a potential barrier between surface and bulk phase. The distribution of ions beneath the monolayer has been shown to follow that originally postulated by Gouy, but our knowledge of the equation of state of an ionised monolayer supported on a solution of electrolyte is as yet far from complete. The rate of transport across oil–water boundaries would evidently be of value in elucidating the problem of cell-wall permeability. I might mention the work of Sjolin on the diffusion of salicylic acid across the benzene–water interface, of Irwin on dyes at the water-chloroform interface, of Hutchinson on alcohols at the benzene–water interface, and of Davies on salts at the nitrobenzene–water interface.

We note that the Nernst partition coefficient K must be equal to the ratio of the specific velocity coefficients across the boundary in both directions, k_{ow} and k_{wo}. The free energy of passage across the interface can be calculated from the expression

$$\frac{1}{k}\sqrt{\frac{\boldsymbol{R}T}{2\pi m}} = \mathrm{e}^{\frac{\Delta F}{\boldsymbol{R}T}}$$

For potassium iodide diffusing from water to nitrobenzene, Davies found $k_{\text{wo}} = 2{\cdot}7 \times 10^{-8}$ cm. sec.$^{-1}$. Inserting the value $m^{0\cdot5} = 8{\cdot}76$, we find, at 25° c, $\Delta F = 15{,}700$ cal./mole. The value of k_{ow} was found to be $1{\cdot}5 \times 10^{-4}$ cm. sec.$^{-1}$, and ΔF is accordingly 10,600 cal./mole. The partition coefficient is evidently $K = \mathrm{e}(\Delta F_{\text{wo}} - \Delta F_{\text{ow}})/\boldsymbol{R}T = 5{\cdot}5 \times 10^{3}$.

Since the activation energy for free diffusion of this salt in water is only 3000 cal./mole, the barrier in moving from water to nitrobenzene is over five times that for free migration. A really reliable method for obtaining true transfer rates is desirable since these preliminary results in which diffusive limitations may not have been entirely eliminated have proved so interesting.

Emulsions form one of the most important classes, as well as one of the oldest, of colloid systems, but their stability and the exact causes of the phenomenon of spontaneous emulsifiction are as yet not clearly understood.

A micelle of a soap in aqueous solution will be stable against further growth because the electrical potential at the interface builds up steeply as more detergent ions enter the already charged surface and this gain in electrical energy balances the energy gained from van der Waals forces acting between the hydrocarbon tails. An invert emulsion, *e.g.*, of soap in paraffin, is likewise stable because clustering of the polar heads, usually in the presence of traces of water, is limited by their mutual electrical repulsion. The interfacial energies in both cases are thus zero. It is clear that a hydrocarbon oil can be introduced into the cluster of hydrocarbon tails constituting the micelle of the first type, this being the process of solubilisation. Up to certain limits the system remains thermodynamically stable and optically clear, although light scattering can be observed with a sensitive photomultiplier tube. The limit is attained when the detergent film on the surface is so distended by the imbibition of the solubilised hydrocarbon between the chains that addition of more soap ions from neighbouring micelles, as well as of oil therefrom, is no longer prevented by the high electrical barrier, so that the solubilising micelles coalesce to emulsion droplets and in due course the system will " break." The invert micelle with oil as the continuous phase will likewise " break " when the addition of sufficient water permits the entry of more soap molecules. Whilst such transport of soap from one emulsion particle to another is possible the emulsion cannot be regarded as stable, and in consequence much attention has been given to the use of insoluble surface-active agents as emulsifiers, *e.g.*, the proteins.

Emulsions stabilised with ionic detergents, although not essentially stable systems, possess a long life since the potential barrier set up is relatively great and may amount to more than 200 mv, the coalescence rate being thereby reduced to less than one ten-thousandth of that expected for uncharged droplets.

We must note that this potential barrier normal to the surface is greater than that portion of it determined by results of shear parallel to the surface, the electrokinetic or zeta potential, which is usually of the order of 50 mv.

Invert emulsions appear to be stabilised by the viscosity of the closely packed hydrocarbon tails, held together by the cluster of hydrated heads. We thus note that emulsion stability involves consideration of the stabilising influence of charge, surface viscosity, surface rigidity, and elasticity, as well as interfacial tension, and the literature reveals that quantitative methods of investigating these factors are now being given active consideration.

Equally important are the questions which have arisen concerning the solid–gas interface. Whilst the distinction between physical adsorption and chemisorption is now generally recognised, there still exists a large difference of opinion in respect to the properties and behaviour of matter in these two states.

Physical-adsorption methods are now generally employed for determination of the specific surface of solids. The various forms of adsorption isotherms of vapours have been frequently interpreted in terms of multilayer formation, but experimental data can as readily be interpreted as the filling of capillaries by condensed liquid. Again the contrasting mechanism of condensation of, say, the vapour of acetone with that of amyl alcohol, where in the former case multilayers are formed and in the latter the sudden appearance of a condensed liquid phase, reveals the danger of generalisation.

Again, for, say, potassium-on-tungsten or toluene-on-mercury surfaces, we have evidence for the growth of a two-dimensional liquid phase at the expense of a surface vapour as the partial pressure of the adsorbent is increased, and we infer that this type of two-dimensional condensation around nuclei of different sizes may be more common that is generally supposed. The expansion of a solid adsorbent which frequently occurs in adsorption is taken as evidence for the view that physically adsorbed species are mobile. It has been suggested that physically adsorbed molecules do not hop from one position to a neighbouring one but can be elevated into a mobile level where they can move for considerable distances along limited paths in the surface atomic valleys, and that the depth of the potential well from the position of rest to the mobile level is of the order of $5\ kT$ or less, a value which would ensure surface migration; this receives support in many directions, such as from observations on the movement of molecules over crystal surfaces and the like, but no really conclusive evidence has been advanced for the extreme view that the adsorbed molecules behave as a free two-dimensional gas in the adsorbed phase.

Similarly in respect to the chemisorbed phase we have during the last decade seen the postulates on which Langmuir founded his famous isotherm equation subjected to close scrutiny. We may remind ourselves that each surface atom was to be regarded as the locus of a valency force, that the adatoms retained fixed positions, and that the adhesion of an adatom was unaffected by its neighbours. Use of freshly formed metallic surfaces in the form either of wires or mirrors, and different methods of determining and evaluating the surface phase such as by measuring the changes produced by contact potential or by photo-electric or thermionic emission, or by alteration of the accommodation coefficient, now give us reasons to believe that these original postulates are not valid, at least for many cases of chemisorption of elementary gases by metals.

Several suggestions have been advanced for modifying the idea of a simple covalent linkage between a metallic substrate atom (*e.g.*, nickel) and, say, a hydrogen atom, whereby the electron from the hydrogen pairs with an electron in the fourth $3d$ orbital. We can assume that a nickel atom situated in the 100 plane has six covalent bonds resonating among eight positions instead of the twelve available to an atom within the crystal. In Pauling's A-type of nickel there are two unpaired $3d$ electron orbitals and, as in palladium, it is one of these that is shared with the hydrogen.

On this view the heat of adsorption of hydrogen on the 100 plane of nickel would be uniform and of the order of 30 kcal. An alternative view is to be noted in which, as electrons are abstracted from the nickel and as the nickel–hydrogen dipoles attain closer proximity to one another, the heat of adsorption, like the thermionic work function, progressively changes. No finality has been reached in these matters, and indeed the mechanism of heterogeneous catalysis even in the simplest of cases is still under active consideration—this in spite of a wealth of experimentation spread over the last thirty years. It was imagined, for example, that on the discovery of deuterium and of radio-isotopes we should be able to gain a further insight into the processes involved. Instead of this, we find that a whole series of new and unsuspected exchange reactions have been revealed indicating, it is true, a new series of possible elementary steps in the catalytic process; and a decisive answer is still awaited.

Again, it might seem to be a simple matter to decide whether in a catalytic reaction between two reactants at a nickel surface both reactants are chemisorbed or only one, a query first raised by Langmuir in 1917. In practice it has been found difficult to give an unequivocal answer, although in the case of catalytic oxidation our information is now more complete.

We have to record much progress in the use of electrophoretic methods for the isolation and separation of biological material such as the enzymes and viruses; for initiation of the preparative work we are indebted to Tiselius. Many of the complexities in the measurement of the electrophoretic velocity of a protein in a buffer salt have been indicated, *e.g.*, the presence of false boundaries and the so-called δ- and ε-stationary boundaries in the ascending and the descending limb of the U-tube. The theory has been worked out in some detail by Svensson, but we cannot yet assign a size, shape, or charge to a protein molecule or determine exactly how these three possible variables change with changing environment.

Thanks chiefly to the work of Professor Kruyt and the Dutch school of colloid chemists, definite advances have to be recorded in our knowledge of the electrokinetics and ionic distribution around ionic crystals.

Silver iodide in which both silver and iodine are the potential-determining ions has been given an exhaustive examination. A silver iodide sol particle has zero charge on it when the concentration of iodine ions in the solutions is some 10^{-10}N, whilst such a sol is stable when the iodine ion concentration is 10^{-5}N; the Nernst potential is thus some 300 mv, and the electrokinetic or zeta potential is some 70 mv. We noted in the case of emulsions a similar ratio between the total transverse potential and the zeta potential of an oil drop. The stability of these sols is clearly not determined by the zeta potential alone. An exhaustive treatment of the interaction between two flat double layers, and also of that between spherical particles, has been given by Verwey and Overbeck who find that the flocculating concentration of added electrolytes varies inversely as the sixth power of the valency, in agreement with the Hardy–Schulz law.

Whilst lattice fit and charge are the two most important properties of the potential-determining ions for the ionic crystals, in the cases of fibres of organic materials such as wool and the synthetic polyamide fibres on the one hand and of cellulose on the other the situation is more complex. It seems clear that the $-NH_3^+$ and to a certain extent the $-CO\cdot NH-$ groups are the ionic accepting groups for the dye anions in the former case and the $-CO_2^-$ and to a certain extent the $-CH_2\cdot OH$ groups (present in cotton) in the latter case, but a comparison of the dyeing properties of a homologous series of dyes indicates that van der Waals contributions from the rest of the molecule, and for cellulose actual adlineation along the cellobiose chain, play an important part in the free-energy change on adsorption.

As in the case of enzymes and of toxins, the configuration and nature of these groups around the actual prosthetic group itself are all-important for specificity, and a systematic attempt to evaluate the free-energy changes on adsorption with molecules in which the groups around some simple prosthetic link are progressively modified both in nature and in spatial orientation does not seem to be beyond our experimental resources. The partition of an ionisable dye between substrate and solution can be treated in two different ways, either by making use of the Donnan distribution between the two phases or by regarding the substrate as containing a number of accessible sites and determining the free-energy change in terms of the fraction of sites occupied. In the former case difficulties arise in computing the volume of the substrate phase. Similar problems arise in respect of the distribution of ions at a monolayer or phase-boundary interface: thus the hydrogen-ion activity beneath a monolayer may differ by as much as one pH unit from that in the bulk phase owing to the adsorptive restraints on the system. The hydrogen-ion distribution can be calculated by means of the Gouy theory, and this non-uniform distribution can be replaced by a uniform distribution in which the Donnan relation between adsorbed and bulk phase is maintained if the depth of the adsorbed phase and thus its volume is computed by the method of Debye and Hückel.

We find both these factors taken into consideration in the treatment of the potential difference between electrolytes separated by sieve-like membranes first examined theoretically in detail by Michaelis. Both Kurt Meyer and T. Teorell regard such membranes as containing a certain number of immobile or fixed ions which renders the membrane positive or negative as the case may be. The concentration of the fixed ions is termed the selectivity constant. The membrane potential is regarded as made up of two Donnan potentials at each interface and a diffusion potential across the membrane itself.

The following table gives some idea of the respective contributions to the membrane potential for a membrane in which the selectivity constant is 1·0 and the electrolyte concentrations (c, c_1) in each side are maintained in the ratio 10 : 1.

c	c_1	Boundary potential (mv)	Diffusion potential (mv)	Total (mv)
100	10	+ 1·1	−13·2	−12·1
10	1	+10·9	−12·1	− 1·2
5	0·5	+20·5	−12·0	+ 8·5
1	0·1	+46·2	− 5·4	+40·8

We have already noted that the colloidal unit according to Graham's definition must on account of its low diffusivity possess a mass weight which is large in comparison with ordinary molecular dimensions. Colloidal particles have indeed been prepared by methods of condensation as well as of dispersion, each particle containing a number of molecular units.

Whilst glues and gelatins were taken to be representative colloids, sufficient information on their state of aggregation and their molecular weights was not available to render them of exceptional interest.

With the realisation that a number of biologically important substances are macromolecular and that it is possible to synthesise, both by polycondensation and by chain reactions, macromolecules of great size, a new and important chapter has been added to our science. We are indebted originally to Staudinger for pointing out that a gradation based upon increasing chain length, giving us crystalloids, hemicolloids, and eucolloids, was possible of attainment.

I need not here digress on the interesting problems concerning macromolecular synthesis which have arisen during the last decade, but we may note as of special interest the various approaches which have been made to the synthesis of polypeptides, to the evaluation of the B and the A terms in the Arrhenius equations for each of the individual steps of the chain reactions involved in chain initiation, propagation, and termination, to the directive influence of groups in linking up asymmetric substituted olefins on the head-to-tail or head-to-head position, and finally to the distribution of units in the chain when interpolymers are formed between two and even three differently substituted olefins.

Unlike the majority of colloid dispersions, the polymer macromolecule possesses inherent flexibility, the degree of which is mainly dependent on the nature of the backbone: thus cellulose and its derivatives are relatively stiff, " Polythene " relatively flexible. The shape of the macromolecule is thus dependent to a great extent on the degree of interaction with the solvent, and in recent years a commencement has been made in evaluating the so-called μ values to characterise this interaction. We must envisage not only Brownian movement of the macromolecular unit but also micro-Brownian movement of segments within the unit itself. The flexible polymers are folded in poor solvents in an irregular manner into a coil, and considerable quantities of solvent can be retained in the macromolecule during its Brownian movement. The contrast between these " solvated " polymers and the relatively stiff " free-draining " macromolecules is clearly exemplified when we come to examine their physical properties in various solvents.

Thus, in the process of diffusion the potential gradient of thermal agitation ($\boldsymbol{k}T$ per molecule) is independent of molecular weight, but the resistance to motion afforded by the statistical coiling of the chain is proportional to the molecular weight for stiff polymers but to the square root of the molecular weight for flexible polymers. In a similar manner the centrifugal sedimentation constant is evidently independent of the molecular weight for cellulosic derivatives but proportional to its square root for flexible rubbers. When we examine flexible polymers by the method of flow birefringence we should expect the latter to be proportional to the rate of shear, up to the point where the shearing stress stretches the individual coils and thus increases the axial ratio of the particle and concomitantly the molecular birefringence.

The fundamental measurable property of solutions is the osmotic pressure. Whilst for a number of colloidal systems the osmotic pressures are too small for measurement we find increasing attention being given to improving the accuracy of determination of osmotic pressures of polymer solutions.

Whilst all matters connected with the osmotic pressures, even of non-ionic polymers, have not yet been clarified we are certain that the simple van't Hoff law

$$\pi = C\boldsymbol{R}T/M$$

is not applicable to these systems which are characterised by a large change in entropy on solution and where the varying extent of polymer–solvent interaction is one of the dominant characteristics; both theory and experiment indicate that the osmotic-pressure equation for polymeric solutions can be written in the form

$$\pi = C\boldsymbol{R}T/M + BC^2\boldsymbol{R}T/M^2$$

where the two parameters M and B are required to define the thermodynamic properties of a polymer in its particular solvent. The parameter B can be expressed in the form $\nu n^2(1 - \mu)^2$ where ν is the molar volume of the solvent, n the number of segments in the macromolecule, and μ the interaction constant.

The following table gives a few of these interaction constants :

	μ
Polystyrene in C_6H_6	0·2
,, PhMe	0·44
,, *n*-butyl laurate	0·74
,, *iso*amyl laurate	0·91

	μ
Rubber in CCl_4	0·28
,, *cyclo*hexane	0·33
,, $CHCl_3$	0·37
,, PhMe	0·43
,, C_6H_6	0·44
,, CS_2	0·49
,, $(C_2H_5)_2O$	0·51
,, $(CH_2Cl)_2$	0·53

It is evident that for a critical value of μ the solution will separate spontaneously into two phases, one rich and one poor in polymer. For large polymers in which n is large the dilute solution may indeed contain very few molecules. Until recently the fact that a strong solution of polymer could apparently co-exist with what was believed to be pure solvent was advanced in support of the assumption of long-range forces. We now know that this view is not correct.

We note also in this connection how the theory of elasticity of randomly coiled deformable networks has been extended to embrace the swelling and imbibition of solvent into deformable cross-linked structures. Here it is possible to determine the degree of swelling when the polymer is in equilibrium with pure solvent.

More recently attention is being given to the properties of ionised macromolecules. Here we can distinguish between two distinct types : those which by internal cross-linking are retained in a compact and regular form, *e.g.*, the native or corpuscular proteins possessing a relatively low viscosity in solution, and those which are freely flexible along their backbone, yielding highly viscous solutions. These would normally take up the random configuration determined by the state of maximum entropy and thus contain free occluded solvent. Owing, however, to the mutual repulsion of the electric charges the sol particle assumes a less probable and more voluminous form, and as a result the specific viscosity is greatly increased—an example of the so-called electroviscous effect. We may observe that amphoteric colloidal macromolecules, *e.g.*, the denatured proteins, will at the isoelectric point suffer contraction owing to the interaction of the " zwitterions," and the sol particle will again assume a less probable but less voluminous form and in consequence will expand on the addition of neutral salts.

We have already observed that, for polymers in non-aqueous solution, when the compatibility constant μ rises to a critical value the system separates into two phases—a polymer-rich and a solvent-rich phase ; similarly, with these hydrophilic ionisable macromolecules a two-phase system is obtained, the polymer-rich phase being designated a coacervate. We are indebted to Bungenberg de Yong for an exhaustive examination of these interesting systems which appear to simulate many biological structures.

During the last twenty years we have obtained a more detailed knowledge of the conditions which determine the relative ease with which macromolecular chains can adlineate with one another and fit into a crystal lattice. With increasing ease of adlineation we can pass successively from rubbers to plastics to fibres. In drawing a macromolecular melt with subsequent cold drawing to form a crystalline fibre, we are interested in the forces between the chain and the energetics of the crystallisation of the units of the chains with one another.

Professor Mark has given the following figures :

Polymer	Molecular cohesion per 5 Å of chain length with co-ordination nos. of 4	
	Unit	Cals.
Polythene	$-CH_2-$	1000
Poly*iso*butylene	$-CHMe-$	1200
Polybutadiene	$-CH_2\cdot CH-$	1100
Rubber	$-CH_2\cdot CH{:}CH-$	1300
Polystyrene	$-CHPh-$	4000
Polychloroprene	$-CH_2\cdot CH{:}CCl-$	1600
Polyvinyl chloride	$-CH_2\cdot CHCl-$	2600
Polyvinyl alcohol	$-CH_2\cdot CH(OH)-$	4200
Polyvinyl acetate	$-CH(CO_2Me)-$	3200
Cellulose	—	6200
Cellulose acetate	—	4800
Polyamides	—	5800
Silk	—	9800

We note the significant increase in molecular cohesion as we proceed from the apolar hydrocarbons to the polar chain systems of the polyamides. For the fibres to acquire mechanical strength the macromolecules must be relatively long, the lower critical length appears to be in the neighbourhood of some 60 monomer units, the strength increasing in a proportionate manner up to some 250 units. Longer chains reveal a further increase in mechanical strength, but the rise proceeds more slowly, attaining a maximum at about 600 units. The following data have been given for commercial polythene :

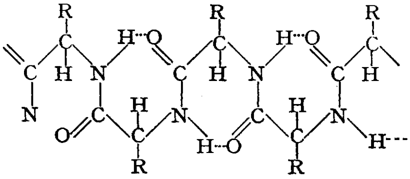
Average mol. wt.	6000	10,500	15,000	21,000
Tensile strength (kg./mm.^{2})	3·5	8·5	10·0	21·0

Whilst with the polymer of ω-hydroxydecanoic acid filaments can be spun but not cold drawn at a molecular weight of 7300. They can be drawn at a molecular weight of 9300 but strong fibres are only attained at 16,000. As the interchain cohesive forces increase, fibre stability attains greater values for lower molecular weights.

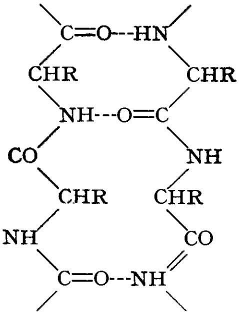
As is well known, fibres can only be drawn from well-defined crystalline material. The fibre symmetry thus becomes an all-important factor. The best example of this factor is doubtless to be found in the glycol esters of phthalic acid where the 1 : 4-acid forms an excellent fibre, the 1 : 3-acid yields a polymer which can just be spun, whilst no form of fibre is obtainable from the 1 : 2-derivative. The same is found for the naphthalene derivatives where the 1 : 5- and the 2 : 6-acid yield excellent fibres, the 2 : 7- is just spinnable and no fibre is obtained from the 1 : 4-compound.

It is clear that the polarizable benzene ring, if in the main chain, exerts a strong interaction with its neighbours, raising the melting point of the crystalline fraction, and forms a good fibre, but, if present as a side chain, its bulk cuts down the interchain interaction to such a small value that the product cannot be drawn into a fibre. It is also much more difficult to cold draw the unsymmetric vinyl $-CH_2{\cdot}CHX-$ polymers than, say, the symmetric vinylidene chloride $-CH_2{\cdot}CCl_2-$ polymer. Indeed, in the latter it is possible to incorporate up to some 20% of a co-polymer without weakening the latent interaction below the point where fibres can be drawn.

In many cases we imagine the chains to be held together by hydrogen bonds. This is well exemplified in the polypeptide fibres where the undrawn or αii modification has, according to Ambrose and Hanby, the following structure :



whilst in the extended or β-form the extended polypeptide chains can form cross links by means of hydrogen bonds:



It is clear that partly extended chains are not capable of making so many cross-links as fully extended chains; thus extension increases to a marked extent the strength of the fibre.

During the last decade progress has been made in the understanding of the properties of fibres in terms of their molecular constitution. Thus, tenacity and flexibility involve deformation of the material; in addition to the usual normal or "Hookean" deformation, fibrous polymers may undergo both elastic and plastic deformation under stress. These displacements can be treated as rate processes, and the correlation between the energies of activation involved and the nature of the polymer, with or without added plasticiser, has opened up new and interesting fields. Again, as we have already noted, fibrous materials may in part be crystalline and the thermodynamic treatment of the conditions of equilibrium of fringed micellar systems permits us to gain some information on the melting range of such polymers.

Colloid science deals with matter in the boundary state. Matter in this state is organised and as a result of such organisation we find many striking co-operative effects. Living matter is likewise organised but in addition it is at its simplest in a state of dynamic equilibrium, more usually in disequilibrium. It remains for those who come after us to study disequilibrium in more detail. As we have seen, a commencement has been made in the study of chemical reaction at interfaces and of transport into and out of the boundary layers. These somewhat jejune attempts are not to be despised, for surely they are beginning to form the pattern of a field of enquiry in which the biologist will be keenly interested.

Finally, I would like to answer those who ask why does one choose to select from the long recognised divisions of science, chemistry, physics, biology, and mathematics, certain selected portions, only to build these up into a rationalised subject with its own peculiarities, its own experimental techniques, and its own intellectual discipline; one might reply that even if colloid science is not satisfying as a basis for a future biology it has undoubted repercussions in an ever increasing number of technological developments: time would not permit one even to list the number and variety of interests from agriculture to zeolites in which the principles of colloid science apply.