CHEMICAL EQUILIBRIUM

THROUGHOUT the history of chemistry two lines of advance may be traced. At one time chemists have endeavoured to answer the question, what does this substance do? At another time they have inquired, of what is this substance composed?

Function and composition have been, and continue to be, the two great guides in the development of chemical science.

Chemistry has always had her kinetical as well as her statical problems.

And in recent times, as dynamical reasonings have been more and more applied to chemical phenomena, we find the broad distinction still prevailing.

"We can already distinguish two lines along which dynamical science is working its way to undermine at least the outworks of chemistry. . . . Of these two lines of advance one is conducted by the help of the hypothesis that bodies consist of molecules in motion, and it seeks to determine the structure of the molecules and the nature of their motion from the phenomena of portions of matter of sensible size. The other line of advance, that of thermodynamics, makes no hypothesis about the ultimate structure of bodies, but deduces relations among observed phenomena by means of two general principles—the conservation of energy, and its tendency towards diffusion" (Clerk-Maxwell, Science Conferences, South Kensington, 1876).

In a paper published in NATURE (vol. xx. p. 530), I endeavoured to give a short sketch of the work of Guldberg and Waage on the influence of mass on chemical action. The theory of these naturalists is largely based on the hypothesis of the molecular structure of bodies and is developed by the application of dynamical reasoning to experimentally determined facts. The theory is a most successful attempt to explain the nature of the motion of certain molecular systems "from the phenomena of portions of matter of sensible size."

Guldberg and Waage deduce the conditions of equilibrium of many representative chemical systems; but they do this by simplifying the phenomena, by considering only the force of affinity, and by overlooking the action of all "secondary forces." They show how chemical equilibrium is modified by changes in the value of the coefficients of affinity, and by changes in the masses of the reacting bodies. They regard each chemical change as proceeding through two or more phases, and as eventually returning to its original phase, and thus completing itself, unless prevented by the action of extraneous forces.

The work of the Norwegian Professors is confirmatory of the kinetic theory of chemical action, that theory, namely, which regards molecular decompositions and recompositions as continuously proceeding even in apparently stable chemical systems.

A most important paper by Prof. Willard Gibbs, of Yale College, bearing on the thermodynamical problem of the equilibrium of chemical systems, appeared some time ago in the *Transactions* of the Academy of Sciences of Connecticut (vol. iii.). This paper was summarised and rendered intelligible to the chemist by the late Prof. Clerk Maxwell in one of those marvellously condensed and suggestive sketches which he, perhaps better than any other naturalist of modern times, knew how to draw. (*loc. cit.*)

Prof. Gibbs deduces from the principles of the conservation and dissipation of energy, a general expression for the stability of any phase of matter with regard to any other phase.

If K represent the stability of a given phase A with respect to any other phase B, then the phase A will tend to pass into the phase B if K is negative; but if K be zero or positive, the phase A is absolutely stable.

K varies with the component masses, volume, and entropy (called *the magnitudes* of the system by Clerk Maxwell), and with the temperature, pressure, and the *potentials* of the component substances (called the *intensities* of the system): "the potential of any component substance is the intensity with which the body tends to expel that substance from its mass."

The phase A may be stable in itself, and, nevertheless, "may have its stability destroyed by contact with the smallest portion of matter in certain other phases."

No absolutely unstable phase can exist for any finite time, but such a phase may form an intermediate stage between other relatively stable phases. Indeed, "the region of absolutely unstable phases is in contact with that of absolutely stable phases at the critical point. Hence, though it may be possible by preventing the body from coming in contact with certain substances to bring it into a phase far beyond the limits of absolute stability, this process cannot be indefinitely continued, for before the substance can enter a new region of stability, it must pass out of the region of relative stability into one of absolute instability, when it will at once break up into a system of stable phases" (Clerk Maxwell, *loc. cit.*).

That certain phases of heterogeneous substances were unstable has, of course, been long known to chemists—although such phases have been almost entirely disregarded in chemical investigations—but we are now taught that not only is the existence of such phases recognised by the great principles of the conservation and dissipation of energy, but that the conditions of their existence, and of their relations to stable phases of the same mass of matter, can be deduced from these principles.

Chemists have long groped after some definite connecting link which should bind their more empirical generalisations with the great principles of energy which are so far-reaching in their application to physical science; the genius of a mathematician seems at last to have revealed the bond.

As examples of what might be called strained equilibrium, that is, of systems carried into phases much beyond the limits of absolute stability, and of the sudden overthrow of the equilibrium by small exciting causes, Prof. Clerk Maxwell notices the case of water, freed from air and surrounded by a liquid of high boiling point, remaining in the liquid state at a temperature much above the boiling point corresponding to the pressure, but exploding instantly it comes in contact with any gas; he also cites the equilibrium of a 37 per cent. solution of calcium chloride when cooled below $-37°$, as described by Guthrie in his researches on cryohydrates.

Many other similar cases might be noted. In my own work I have recently met with certain phenomena which may, I believe, be explained by the general principle now under consideration.

In studying the effects of mass, time, &c., on the decomposition which may be formulated—

$$x \, BiCl_3 + x' \, HCl + x'' \, H_2O = (x-n) \, BiOCl + n \, BiCl_3 + \{x' + 2(x-n)\} \, HCl + \{x'' - (x-n)\} \, H_2O,[1]$$
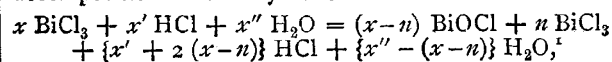
I noticed that if such a quantity of water be cautiously poured on to the surface of a solution of bismuthous chloride in hydrochloric acid, as just suffices to produce a trace of solid bismuthyl chloride (BiOCl) at the surface of contact of the two liquids, and if the liquids be then mixed, the amount of bismuthous chloride which has undergone decomposition after a given time—provided the time be short—is much more than if the water be added to the bismuth solution with constant stirring.

Indeed, I found that it was possible to arrange two systems, each containing the same quantity of $BiCl_3$, HCl, and H_2O, so that one of these should remain clear, *i.e.*, without formation of BiOCl, whilst in the other a considerable amount of decomposition should occur.

[1] Chem. Soc. *Journal, Proc* 1879, p. 311.

The explanation of this phenomenon put forward in the paper alluded to was founded on the molecular hypothesis; but I think that a fuller explanation is afforded by the results of Prof Gibbs's investigations.

When the water was added on the surface, a small quantity of the matter in the vessel instantly passed into another phase; this being in contact with matter in the original phase, induced therein a phase of relative instability, and this succession of phases proceeded until a new condition of stable equilibrium was attained. The entropy of the system was altered by the production of small quantities of BiOCl; K would almost certainly be negative for the new phase with regard to the original phase, and therefore the original phase would become unstable by contact with it of a small portion of matter in the new phase. If, however, the formation of matter in the new phase were prevented by the special contrivance of adding the water in a peculiar way, then the original phase would be stable, if, however, a somewhat large quantity of water were added, the whole system might be carried much beyond the limits of absolute stability without overthrow of equilibrium, but this equilibrium would necessarily eventually be overthrown, as was indeed always found to be the case.

In a paper recently published in the *Journal* of the Chemical Society in conjunction with Mr. Slater, of St. John's College, I detailed the results of an examination of the influence exerted by variations in the amount of water of dilution on the chemical change formulated—

$$BaCl_2 + K_2C_2O_4 = BaC_2O_4 + 2KCl.$$
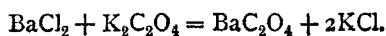
It is there shown that the progress of this change is retarded to a proportionately greater extent by a large, than by a small quantity of water of dilution, and that this retardation is especially marked when the action proceeds at low temperatures. In order to explain this result we suggested the hypothesis that when much water is present and a low temperature is maintained various hydrates of barium chloride, especially the cryohydrate ($BaCl_2.37H_2O$ solidifying at $-8°$), are produced, and that these, being formed in presence of a large mass of one of the products of their own dissociation, are comparatively stable. We discuss and illustrate this hypothesis in the paper, and, in our opinion, establish for it a fair degree of probability.

Now, if this hypothesis be granted, I think we have in these experiments another illustration of the general principle laid down by Prof. Gibbs.

If $BaCl_2 + K_2C_2O_4$ be called phase A of the system, then undoubtedly K is negative with regard to $BaC_2O_4 + 2KCl$, *i.e.*, with regard to phase B. Phase A is absolutely unstable, and tends to pass into phase B. But during this passage a phase, or phases, is reached which is only relatively unstable. Could the matter in this phase (which may be called the cryohydrate phase) be separated from that portion already in phase B, the intermediate phase might become absolutely stable; this, however, is not done, and hence the whole system tends to pass into phase B. But it is evident that those conditions which favour the formation of matter in the cryohydrate phase must also retard the passage of the system into phase B. Moreover, while the system is in the cryohydrate phase, it is carried to a certain extent beyond the limits of absolute stability, and if this phase were abnormally extended we should expect to obtain a condition of unstable equilibrium liable to complete overthrow by small exciting causes. In the paper referred to we show that such an expectation can be realised.

A class of reactions in chemistry, hitherto treated for the most part as isolated facts, seems to find its explanation in the generalisation now established by the Yale Professor, viz., that the equilibrium of matter in a relatively stable phase may be overthrown by contact with even very small portions of matter in another phase.

As examples of the reactions referred to may be cited, the decomposition of ozone by silver, and of barium peroxide by platinum; the production of diphenylmethane from benzene and benzylic chloride only in presence of a small quantity of zinc or copper; the action of hydrochloric acid on bismuthous oxide in presence of a small quantity of water;[1] and in general those numerous reactions which are modified by the presence of traces of foreign substances.

In other cases contact with small quantities of matter in another phase appears to retard the passage of the main system from its initial phase to a phase of greater stability. Thus Bunsen and Roscoe showed[2] that the resistance to combination of a mixture of hydrogen and chlorine when exposed to sunlight is increased by the presence even of traces of oxygen.[3]

Every chemical system thus appears to tend towards a phase of maximum stability. If the entropy of the system be decreased, K will be increased in the general equation of Gibbs, and hence the stability of the system will be increased.

All chemical systems not in phases of absolute stability will therefore tend to lose entropy.

This is probably a better method of stating Berthelot's so-called *law of maximum work* than that generally employed.

Moreover, it may be possible to convert a phase of absolute stability into a phase of relative stability, and thence into a phase of absolute instability, by contact with matter in another phase, *i.e.*, in ordinary chemical language, by the action of a reagent.

The readiness with which so many chemical systems undergo change leads one to ask whether chemical systems are not generally in one or other of those phases of relative instability which are so easily overthrown by contact with small quantities of matter in other phases. If this be so, and if it be granted as extremely probable, that even apparently stable systems are passing through cycles of change, then we should expect that slight changes in the values of the "magnitudes" or "intensities" of chemical systems would in many cases induce the overthrow of the stability of these systems.

The considerable differences in the properties of many carbon compounds as described by different experimenters, may not improbably be due to the changes induced in these bodies by contact with small traces of impurities, *i.e.*, of matter in phases other than that of the main portion of the system.

The more complex the possible actions and reactions in any given system of heterogeneous substances, the more probable will be the occurrence of unstable phases, and the more will the course of what we call the chemical change be turned aside by small variations of the "magnitudes" or "intensities" of the system.

In chemical changes involving few intermediate phases —or to put it in another way, in chemical changes wherein the action of "secondary forces" is small—the course of the change may be followed, and generalisations made concerning it, as was done by Harcourt and Esson for a special case.[4] When the action becomes a little more complex, we appear to gain the conditions under which so-called "chemical induction" becomes possible; while from the study of exceedingly complex actions no generalisations can be safely deduced.

This view of chemical systems as readily undergoing change when in contact with other systems, and of these changes as being dependent on the energy of the systems

1 Examined by me in Chem. Soc. *Journ.*, 1879; *Proc.*, p. 336.
2 *Phil. Trans.*, 1856.
3 The modifying influence exerted on a process of chemical change by the presence of a foreign substance was considered in 1850 by Brodie, in an able paper, in which, speaking of the decomposition of barium peroxide by platinum, he says: "The platinum causes that chemical relation between the particles which renders the decomposition possible."
4 Chem. Soc. *Journ.*, xx. 460.

in different phases, may lead to a fuller explanation of the "acceleration coefficients" of Harcourt and Esson. These chemists found that the change formulated

$$H_2O_2 + 2HI = 2H_2O + I_2$$
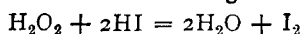
was accelerated to a definite extent by addition of sulphuric or hydrochloric acid, but that the accelerating value of each acid was different. The "acceleration coefficients," which they suggested might profitably be found for classes of salts, would measure the changes in the energies of the systems, brought about by the addition of the salts used.

The work of Prof. Gibbs will probably tend to modify the views generally held with regard to the meaning of constitutional or structural formulæ, and to lead us to regard these formulæ as crude representations of the configuration of the molecule when it has passed into the phase preceding that of absolute instability, rather than of its configuration when it is unacted on by matter in a phase different from its own, and is therefore itself in a phase of absolute stability.

Of course the possibility of predicating a general decomposition for a group of compounds, shows that these compounds all tend to pass—under the influence of one and the same reagent—into analogous unstable phases, and that their structure, before contact with the reagent, is therefore probably analogous.

Prof. Gibbs has shown how the laws of energy may be applied to the solution of chemical problems, and in doing this he has opened a new path of advance, and has supplied a guide long sought for by students of chemistry.

M. M. PATTISON MUIR

A LEAF FROM THE HISTORY OF SWEDISH NATURAL SCIENCE [1]

I.

BEFORE the Era of Freedom (1721, 1772) Sweden had produced only four men who had earned for themselves a recognised name in the history of the natural sciences by discoveries in the field of natural research. These were Sigfrid Aron Forsius,[2] unfortunate in his predictions, author of a Mineralogy which had an extensive sale, but is full of superstition, and did not advance the science in any noteworthy degree; the quarrelsome and whimsical Upsala professor, Olof Rudbeck,[3] who, at the age of twenty-five, published his discovery of the lymphatic vessels; the physician of European reputation, Urban Hjaerne,[4] superintendent of one of the first State laboratories established for *scientific* investigation, famous for his researches regarding mineral waters, the increase of weight in metals on their oxidation, and formic acid, the discoverer of several new minerals, &c.; the afterwards so renowned mystic Emanuel Swedenborg,[5] known in the history of the natural sciences for various geological treatises of great excellence, considering the period when they were written, for a remarkable work on atomicity, for several crystallographical researches, for the largest and most complete handbook on metallurgy, &c.

These formed the whole contribution that Sweden, during her period of greatness, was able to make in this

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[1] Translated from a paper by Prof. A. E. Nordenskjöld, of Stockholm.
[2] Born at Helsingfors after the middle of the sixteenth century; died 1637.
[3] Born 1630, died 1702. His discovery of the lymphatic vessels was published in 1653.
[4] Born 1641; died at Stockholm in 1724.
[5] Swedenborg was born in 1688; died in 1772. The greater portion of his period of activity therefore falls under the Era of Freedom, but most of his scientific works were published before 1721, among them his "Prodromus Principiorum Rerum Naturalium," in which, among other things, he attempts to explain the physical properties of bodies, on the supposition that they are composed of an endless number of minute atoms. His great metallurgic works were first published in 1734. In the *Transactions* of the Royal Academy of Sciences he published, as late as 1763, a "Description of a Method of Inlaying Tables and other Furniture with Marble," free from all mysticism. The table described in this paper is still preserved at the office of the Swedish Board of Trade.

field. Here up in the remote north we had, as far as scientific research is concerned, remained completely undisturbed by the discoveries of Copernicus, Descartes, Leibnitz, and Newton, nay, even the original researches of Danish men of science such as Tycho Brahe, Steno, Bartholinus, and Roemer, had awakened no *fruitful* response on our side of the Sound.

There came, however, another period. Our short dream of greatness had come to a bloody termination. Of the Sweden formerly so powerful there remained but a maimed, depopulated nucleus, impoverished by perpetual war, whose part in the labour of the development of the race appeared to have been long ago played out. No glorious interference in the field of politics was any longer possible. But instead there began here, in the peaceful field of science, labours attended with such success that the history of other countries can scarcely show anything corresponding to it.

Our native country, where, as I have just pointed out, there was previously scarcely any scientific research, was for two decades after the peace of Nystad (1721) as fruitful in this field as any cultured state whatever, and some ten years later occupied the first rank in zoology and botany through Linnæus, in mineralogy through Wallerius and Cronstedt, in chemistry through Brandt, Cronstedt, Scheffer, Bergman, Scheele. There were also valuable contributions to the development of physics from Wassenius, Klingenstjerna, Hjorter, Celsius, Wargentin, Wilke, &c., and to the knowledge of our globe through Bergman's excellent "Description of the Globe," and the travels of the numerous pupils of Linnæus. Remarkably enough, this period of greatness in the field of research is almost conterminous in time with that "Era of Freedom" which is often depicted in so dark colours by our writers of history. It was clearly born of the spirit which accompanied the new constitution, and it got its death blow at the revolution by which Gustavus III. is said to have "saved the country."

The object of this paper is to contribute to the history of our civilisation a sketch of the influence which Swedish men of science of that age exerted on the development of chemistry and mineralogy.

The line of the great men of science from that period is headed by George Brandt, Councillor of Mines and Superintendent of the Laboratory of the Mining Board at Stockholm (born 1694, died 1768).

During the seventeenth century and the beginning of the eighteenth most of the writings of authors on chemistry still contain an unintelligible confusion of endless considerations concerning the way in which the bodies on the earth's surface are composed of certain supposed primitive substances, for instance, according to the school of Aristotle, of fire, earth, water, and air; according to Basil Valentine and Paracelsus, of certain elementary principles—salt, sulphur, and quicksilver. The service of having shown the groundlessness of these fancies is to be ascribed to the great English *savant*, Robert Boyle (died 1691). In opposition to his predecessors, he laid down the fundamental principle that the chemist ought to consider every body as simple which with the means at his disposal he cannot chemically decompose, a principle which indeed took from chemistry much of the glitter of learning with which it before was bedecked, and which in the eyes of philosophers reduced this science to an art of cookery, which in any case, when the old creations of fancy, constructed with so much trouble and subtlety, were blown away, gave the science a stable foundation to build on. Boyle's fundamental principle has since been further developed, and now forms one of the corner-stones of the modern chemistry—although it must be admitted that it is little in accordance with the simplicity which otherwise prevails in nature, that the material world should consist of more than sixty different elements. Certain it is in any case that the elements in question, at least for the