about 150 mgr. of radium was introduced and left for three days. This should lead to the production of about $\frac{1}{10}$ c.mm. of helium. We have seen that in these experiments we could detect with certainty a quantity of neon less than $\frac{1}{1000}$ c.mm. Consequently, even supposing that the emanation does change into neon, the amount so produced cannot be more than one per cent. of the helium which is also formed. Cameron and Ramsay were apparently not aware of the delicacy of the spectroscopic detection of neon in small quantities of air. In the experiment described in their last paper, they state that they were unable to avoid a leakage of air into their apparatus, and working with 12.6 c.c. of mixed gases, they found after the removal of hydrogen and oxygen that the residue consisted of .292 c.c. of nitrogen and carbon dioxide. Assuming that this residue consisted mainly of nitrogen, it would show that there was a leakage of air of about .36 c.c. In our experience, the admission of such a quantity of air into the apparatus gives a brilliant spectrum of neon comparable in brightness with the companion helium spectrum. Consequently, the experiment described by Cameron and Ramsay is quite inadequate as a proof of the production of neon from the emanation.

University of Manchester,
Oct. 6, 1908.

LXVIII. *On the Equilibrium of Heterogeneous Substances*
(1876). *By the late Prof. J. CLERK MAXWELL, F.R.S.*

[THE paper here reprinted is the report of an Address delivered by Prof. Clerk Maxwell on May 24, 1876, at the South Kensington Conferences in connexion with the Special Loan Collection of Scientific Apparatus. It is contained (pp. 144-150) in the official volume of reports of the Conferences, which has long ago dropped out of notice. An earlier and less complete version of this summary of Prof. Willard Gibbs's developments of the doctrine of available energy, on the basis of his new concept of the chemical potentials of the constituent substances, was communicated to the Cambridge Philosophical Society on March 8, 1876, and appeared in abstract in vol. ii. of their Proceedings, pp. 427-430; it was reprinted in Maxwell's 'Collected Papers,' vol. ii. pp. 498-500. The fact that the energy associated with any constituent substance is proportional jointly to the mass of that constituent and to another factor representing energy per unit mass, is of course involved in the very notion of conservation of energy; but the general factorization into magnitudes (or quantities) and intensities

(such as the potentials of Gibbs) is, it would seem, here set forth formally and explicitly for the first time, though it is thoroughly implied throughout Gibbs's work. This paper reviews only the first portion of that work, Proc. Connecticut Academy, Oct. 1875–May 1876; the second part of it, mainly special applications, did not appear in the same Proceedings until May 1877–July 1878. The principle, as restated in less guarded terms by G. Helm (1887), that each type of (available) energy strives to pass from positions of higher to positions of lower intensity, has been supposed sometimes to mark a new departure in physical ideas: cf. Prof. W. Ostwald, *Die Energie* (1908) p. 103, whose regret, expressed in this connexion, that he has not had access to Maxwell's paper, has revived the project of re-printing it. Some years before this time, in a paper "On the Mathematical Classification of Physical Quantities," Proc. Lond. Math. Soc. vol. iii., Maxwell had pointed out, in connexion with Rankine's idea of factors of energy, that this conception loses most of its definiteness and efficacy when applied to kinetic phenomena. It is only for static or steady material transformations that it is effective; and it became so, in development of the general Kelvin doctrine of available energy, only by virtue of the fundamental step involved in Gibbs's recognition of the existence of quantitative chemical potentials for the independent constituent substances of a mixture or solution,—involving the formulation of the general criterion of chemical coexistence of complex substances in contact, that the potential of each constituent should be the same in both of them, and of the trend of chemical change, towards positions of lower aggregate potential.

Most interesting also as regards this evolution of ideas is the postscript of a letter from Maxwell to Stokes of an earlier date, August 3, 1875, in which, in connexion with Andrews's experiments on the condensation of mixed gases, Maxwell sends a tentative sketch of the whole theory, using a provisional term *reaction*, printed between inverted commas, for the quantity which his friend Gibbs soon afterwards named chemical *potential*: see 'Memoir and Scientific Correspondence of Sir G. G. Stokes,' vol. ii. pp. 33–35 (Cambridge, 1907).—J. LARMOR.]

THE warning which Comte addressed to his disciples, not to apply dynamical or physical ideas to chemical phenomena, may be taken, like several other warnings of his, as an indication of the direction in which science was threatening to advance.

We can already distinguish two lines along which dynamical science is working its way to undermine at least the outworks of Chemistry, and the chemists of the present day, instead of upholding the mystery of their craft, are doing all they can to open their gates to the enemy.

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. The thermodynamical problem of the equilibrium of heterogeneous substances was attacked by Kirchhoff in 1855, when the science was yet in its infancy, and his method has been lately followed by C. Neumann. But the methods introduced by Professor J. Willard Gibbs, of Yale College, Connecticut *, seem to me to be more likely than any others to enable us, without any lengthy calculations, to comprehend the relations between the different physical and chemical states of bodies, and it is to these that I now wish to direct your attention.

In studying the properties of a homogeneous mass of fluid, consisting of n component substances, Professor Gibbs takes as his principal function the energy of the fluid, as depending on its volume and entropy together with the masses, $m_1, m_2, \dots m_n$ of its n components, these $n+2$ variables being regarded as independent. Each of these variables is such that its value for any material system is the sum of its values for the different parts of the system.

By differentiating the energy with respect to each of these variables we obtain $n+2$ other quantities, each of which has a physical significance which is related to that of the variable to which it corresponds.

Thus, by differentiating with respect to the volume, we obtain the pressure of the fluid with its sign reversed; by differentiating with respect to the entropy, we obtain the temperature on the thermodynamic scale; and by differentiating with respect to the mass of any one of the component substances, we obtain what Professor Gibbs calls the potential of that substance in the mass considered.

As this conception of the potential of a substance in a

* Transactions of the Academy of Sciences of Connecticut, vol. iii.

given homogeneous mass is a new one, and likely to become very important in the theory of chemistry, I shall give Professor Gibbs's definition of it.

"If to any homogeneous mass we suppose an infinitesimal quantity of any substance added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass, divided by the mass of the substance added, is the potential of that substance in the mass considered."

These $n + 2$ new quantities, the pressure, the temperature, and the n potentials of the component substances, form a class differing in kind from the first set of variables. They are not quantities capable of combination by addition, but denote the intensity of certain physical properties of the substance. Thus the pressure is the intensity of the tendency of the body to expand, the temperature is the intensity of its tendency to part with heat; and the potential of any component substance is the intensity with which it tends to expel that substance from its mass.

We may therefore distinguish between these two classes of variables by calling the volume, the entropy, and the component masses the *magnitudes*, and the pressure, the temperature, and the potentials the *intensities* of the system.

The problem before us may be stated thus:—Given a homogeneous mass in a certain phase, will it remain in that phase, or will the whole or part of it pass into some other phase?

The criterion of stability may be expressed thus in Professor Gibbs's words:—"For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.

"The condition may also be expressed by saying that for all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be negative."

Professor Gibbs has made a most important contribution to science by giving us a mathematical expression for the stability of any given phase (A) of matter with respect to any other phase (B).

If this expression for the stability (which we may denote by the letter K) is positive, the phase A will not of itself pass into the phase B, but if it is negative the phase A will of itself pass into the phase B, unless prevented by passive resistances.

The stability (K) of any given phase (A) with respect to any other phase (B), is expressed in the following form :—

$$K = \epsilon - vp + \eta t - m_1\mu_1 - \&c. - m_n\mu_n,$$

where ϵ is the energy, v the volume, η the entropy, and $m_1, m_2, \&c.$ the components corresponding to the second phase (B), while p is the pressure, t the temperature, and $\mu_1, \mu_2, \&c.$ the potentials corresponding to the given phase (A). The intensities therefore are those belonging to the given phase (A), while the magnitudes are those corresponding to the other phase (B).

We may interpret this expression for the stability by saying that it is measured by the excess of the energy in the phase (B), above what it would have been if the magnitudes had increased from zero to the values corresponding to the phase B, while the values of the intensities were those belonging to the phase (A).

If the phase (B) is in all respects except that of absolute quantity of matter the same as the phase (A), K is zero ; but when the phase (B) differs from the phase (A), a portion of the matter in the phase (A) will tend to pass into the phase (B) if K is negative, but not if it is zero or positive.

If the given phase (A) of the mass is such that the value of K is positive or zero with respect to every other phase (B), then the phase (A) is absolutely stable, and will not of itself pass into any other phase.

If, however, K is positive with respect to all phases which differ from the phase (A) only by infinitesimal variations of the magnitudes, while for a certain other phase, B, in which the magnitudes differ by finite quantities from those of the phase (A), K is negative, then the question whether the mass will pass from the phase (A) to the phase (B) will depend on whether it can do so without any transportation of matter through a finite distance, or, in other words, on whether matter in the phase B is or is not in contact with the mass.

In this case the phase (A) is stable in itself, but is liable to have its stability destroyed by contact with the smallest portion of matter in certain other phases.

Finally, if K can be made negative by any infinitesimal variations of the magnitudes of the system (A), the mass will be in unstable equilibrium, and will of itself pass into some other phase.

As no such unstable phase can continue in any finite mass for any finite time, it can never become the subject of experiment ; but it is of great importance in the theory of

chemistry to know how these unstable phases are related to those which are relatively or absolutely stable.

The absolutely stable phases are divided from the relatively stable phases by a series of pairs of coexistent phases, for which the intensities p , t , μ , &c. are equal and K is zero. Thus water and steam at the same temperature and pressure are coexistent phases.

As one of the two coexistent phases is made to vary in a continuous manner, the other may approach it and ultimately coincide with it. The phase in which this coincidence takes place is called the Critical Phase.

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.

Thus in water for any given pressure there is a corresponding temperature at which it is in equilibrium with its vapour, and beyond which it cannot be raised when in contact with any gas. But if, as in the experiment of Dufour, a drop of water is carefully freed from air and entirely surrounded by liquid which has a high boiling-point, it may remain in the liquid state at a temperature far above the boiling-point corresponding to the pressure, though if it comes in contact with the smallest portion of any gas it instantly explodes.

But it is certain that if the temperature were raised high enough the water would enter a phase of absolutely unstable equilibrium, and that it would then explode without requiring the contact of any other substance.

Water may also be cooled below the temperature at which it generally freezes, and if the water is surrounded by another liquid of the same density the pressure may also be reduced below that of the vapour of water at that temperature. If the water when in this phase is brought in contact with ice it will freeze, but if brought in contact with a gas it will evaporate.

Professor Guthrie has recently discovered a very remarkable case of equilibrium of a liquid which may be solidified in three different ways by contact with three different substances. This is a solution of chloride of calcium in water

containing 37 per cent. of the salt. This solution is capable of solidification at -37°C. , when it forms the solid cryohydrate having the same composition as itself. But it may be cooled somewhat below this temperature, and then if it is touched with a bit of ice it throws up ice, if it is touched with the anhydrous salt it throws down anhydrous salt, and if it is touched with the cryohydrate it solidifies into cryohydrate.

LXX. *On the Atomic Weight of Radium and other Elementary Substances.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN the paper which you were good enough to reprint from the Memoirs and Proceedings of the Manchester Literary and Philosophical Society in the Magazine of February last, it was shown from the definite multiple relations of the first and second series of elements, Hn and $\text{H}2\text{n}$, that radium was the next higher member to barium of the alkaline earth metals, with an atomic weight of 184 and a proximate specific gravity of 5.

The numerical relations of these series are of so much interest and importance to chemical science, especially in regard to the evolution of elementary substances, that I should like to place on record in the Philosophical Magazine the method by which the atomic weights of the first three series have been determined. Also my complete Table of the elements with their atomic weights, in order to elucidate the subject of this communication and for future reference.

Hn.	$\text{H}2\text{n.}$
$\text{H} = 1$	$\text{He} = 2$
$0.0.7 = \text{Li} = 7$	$0.0.8 = \text{Gl} = 8$
$1 \times 23.0 = \text{Na} = 23$	$1 \times 24.0 = \text{Mg} = 24$
$2 \times 23 - 7 = \text{Ka} = 39$	$2 \times 24 - 8 = \text{Ca} = 40$
$3 \times 23 - 7 = \text{Cu} = 62$	$3 \times 24 - 8 = \text{Zn} = 64$
$4 \times 23 - 7 = \text{Rb} = 85$	$4 \times 24 - 8 = \text{Sr} = 78$
$5 \times 23 - 7 = \text{Ag} = 108$	$5 \times 24 - 8 = \text{Cd} = 112$
$6 \times 23 - 7 = \text{Cs} = 131$	$6 \times 24 - 8 = \text{Ba} = 136$
$7 \times 23 - 7 = x = 154$	$7 \times 24 - 8 = x = 160$
$8 \times 23 - 7 = x = 177$	$8 \times 24 - 8 = \text{Ra} = 184$
$9 \times 23 - 7 = \text{Hg} = 200$	$9 \times 24 - 8 = \text{Pb} = 207$

It will be seen that if the second member of the series Hn ($\text{Na}23$) be multiplied by an arithmetical series, then will