ART. XXXVIII.—*Some additional Notes on Argon and Helium;* by EDWIN A. HILL.

AN English scientist in a recent letter, referring to the point made in my article on argon,* as to the inconsistency of regarding a free or nascent monatomic atom as devoid of chemical affinity, asks the very pertinent question whether I have considered the case of mercury vapor, which at 800° is monatomic and yet has practically no chemical affinity. I had indeed given this case some consideration, but lack of space kept me from referring to it in my previous article.

Lord Rayleigh and Prof. Ramsay, in their original memoir, use the following language: "In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although monatomic, forms compounds which are by no means stable at a high temperature in the gaseous state, and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements." The assumption evidently being, that at all ordinary temperatures, argon is heated to a point above that at which chemical affinity is strongly manifested.

Of course argon may yet prove to be either a mixture or a compound of elements, but assuming it to be a single element, the important question still remains unsettled as to the number of atoms comprising its molecule.

The ratio of the two specific heats, as derived from experiments on the velocity of sound in argon, has been shown to be about 1·65, approximating closely to 1·67, the value which, according to the theory of Clausius, proves the gas to have no energy of rotation. The conclusion, that therefore the gas is monatomic, depends on at least three things:

1st. On the correctness of the assumption that a gas, with *little* or no rotational energy, cannot be di- or *n*-atomic, but must be monatomic. In my article on argon (l. c.) I have endeavored to show, that the amount of rotational energy acquired by gaseous molecules will depend on the relation between the repulsive forces acting during the encounter, and the attractive forces aggregating the atoms into a molecule; and that even if the rotational energy be but slight, di- or *n*-atomicity may be possible, and monatomicity does not therefore necessarily follow.

2d. The conclusion also depends upon the correctness of the deduction of Clausius, that a ratio of the two specific heats of 1·67 proves the gas to have no rotational energy. This is

* This Journal, May, 1895, p. 413.

questioned by C. E. Basevi (Nature, July 4, 1895, p. 221), who endeavors to show that the equation $\beta = \frac{2}{3}\frac{1}{\gamma-1}$ of Clausius should be written $\beta = 3k(\gamma-1)$, where $\beta =$ the number of atoms in the gaseous molecule. This latter equation he shows gives 2 for the value of β in argon, leading to the conclusion that argon is diatomic; the mathematical proof being given in full.

3d. The conclusion also depends upon the correctness of the method for calculating the ratio of the two specific heats. This ratio, it will be remembered, was obtained indirectly from the velocity of sound in argon gas, as determined by the "Kundt" dust figures. Dr. G. Johnstone Stoney,* in a paper read before the Royal Society, May 20, 1895, doubts the correctness of the method employed in this determination, and advances proof in support of the position that the ratio 1·65, thus determined, is not the true ratio of specific heats; and if so it is of course not yet shown that argon gas has no rotational energy, and the argument for its monatomicity fails.

4th. Moreover Prof. B. Brauner remarks:† "It has been shown most ably by Mendelèeff, that the argument derived from the relation of specific heats = 1·66 is not absolutely conclusive in favor of the monatomicity of the gases in question (argon and helium).‡ Practically the same point was made independently by myself in my previous article (l. c., pp. 409–410) and also foot note quoting Mendelèeff, whose remarks came to my notice after that article was in press.

Now all of these points may be well taken, or some may be sustained and others not, *but if any one of them is sustained the argument for monatomicity fails.* The fact is that monatomicity seems to most careful thinkers utterly inconsistent with the classification of Mendelèeff, as well as all the various modifications of it which have appeared from time to time. There seems to be a deep-seated feeling that something remains to be explained; that the general principles upon which Newlands, De Chancourtois, Mendelèeff, Meyer, and the host of others have based their classifications, are in the main correct; and that argon fails to find its place in these classifications because some of our preconceived notions of the molecule need to be modified; and hence the foregoing attempts. At any rate, such are the views which impelled me to publish my own article on argon and the periodic law.

* Nature, July 18, 1895, p. 286, and Proc. Roy. Soc., vol. lviii, p. 177. Nature gives an abstract only.

† Chemical News, June 7, 1895, p. 271.

‡ See Proc. Russian Chem. and Phys. Soc., March 2 (14), 1895; Nature, vol. li, p. 543, and Chemical News, July 12, 1895, p. 14.

Now the pertinency of the question about argon and mercury vapor is this. Every fact which seems to be against the theory of monatomicity increases the probability that some one or more of these various explanations of the apparent inconsistency between the specific heat ratio and the conclusions drawn from the Periodic Law, may be correct. These explanations have not all the certainty of geometrical demonstrations, and if the verdict on them is, for instance, "*very probable but not fully proven*," then every additional argument strengthens the probability.

Of course, by far the strongest argument against monatomicity is the Periodic Law, but what we are looking for, I take it, is additional evidence.

I have already remarked (l. c., p. 412–413) that the nascent or monatomic state of the element is, par excellence, that in which chemical affinity has its maximum development, and that all our chemical experience leads us to associate chemical affinity with the free and uncombined atom. Why then, if argon be monatomic, that is free and uncombined, has it no chemical affinity at ordinary temperatures?

Because (it is replied), at those temperatures it is already heated above the point at which chemical combination is possible, and as when we cool mercury vapor from 800° down towards the point at which it assumes the liquid state, it begins to exhibit chemical affinity, so were argon likewise cooled down towards the point at which it begins to liquefy (−189·6°), it also would probably exhibit chemical affinity. Now even were this true, the monatomicity of argon would not thereby be directly proven; we should merely have removed one great and almost insuperable objection against the monatomic theory. But on the other hand, if it be not true, then it would be very difficult, if not impossible, to still hold the monatomic theory. Unfortunately, thus far no experiments have been published showing whether or not argon, near the low temperature at which it becomes liquid, exhibits chemical affinity.* Were this shown to be so, the case for monatomicity would be thus far strengthened, in that a great objection to the theory would have been removed; but our present knowledge of the properties of argon does not lead us to expect the display of any such affinities, for the only approach to an argon compound thus far made has been effected by apparently increasing

* The suggestion that argon compounds will only be formed at low temperatures, which follows directly from the assumption as to argon being too hot to combine, was made in the Educational Times, April 1, 1895, p. 479, and by Mr. C. J. Reed, Chem. News, May 3, 1895, p. 213.

instead of decreasing the energy of the gas (combination with benzene).*

There are, however, some experiments which seem to point against the monatomic theory. Thus Lord Rayleigh remarks as follows:† "It has turned out that the gas possesses the same value of $\frac{PV}{T}$ as hydrogen, and that the value of this expression is not altered between $-90°$ and $+250°$ . . . . Argon therefore shows no signs of association on cooling nor of dissociation on heating." The inference is that like change of temperature would have no greater effect on its chemical affinity than on its state of molecular aggregation.

In the absence, however, of direct experiment to determine the point, we may pursue an indirect method. If we can, from the known properties of argon, determine the class of bodies to which it belongs and with which its greatest analogies are found, then whatever we can predicate of these bodies as a class, we can within reasonable limits predicate of argon also. If they, as a class, are at ordinary temperatures far below instead of above the point at which chemical affinity is overpowered by heat, then probably argon is likewise below rather than above that point; and if below, then the theory of its monatomicity has before it the very difficult task, of explaining away the lack of chemical affinity in the free atom of argon.‡

Of course if the molecule is di- or *n*-atomic, its chemical inertness, like that of N^2, is readily explained by the strength of the force aggregating the atoms in the molecule, which force opposes chemical affinity, since the force of affinity must first disintegrate the molecule before combination with other atoms can take place, that is, must first overcome the force of molecular aggregation.

In general we may say of molecules, that starting with the minimum of heat in a solid and inactive state, as they acquire heat energy they become successively liquid, gaseous, and are

* And I may add Berthelot's combination with carbon disulphide, and more recently, Prof. Ramsay's combination with incandescent carbon, Chem. News, Aug. 2, 1895, p. 51; in all which cases a large quantity of electrical energy is needed to bring about the combination.

† Nature, June 6, 1895, p 127.

‡ It may occur to some that should argon prove a mixture of gases, the argument fails, and as the evidence favors the mixture theory, the argument has but little weight. The conclusion, however, is incorrect. If argon is a mixture, its components are gases which resemble each other in chemical and physical properties so closely, that up to the present time no method of separating them has been discovered. Hence any inference as to the properties of this mixture, which we call argon, must apply with equal correctness to all constituents present in quantity. But if argon is a mixture, the apparent conflict with the periodic law may be explained by the presence of two gases, of different densities, but similar chemical and physical properties.

finally dissociated into atoms. The force of molecular aggregation is a maximum when heat energy is a minimum. With increase of temperature the force of aggregation between like atoms (as I and I for example) is finally weakened, so that in the liquid or gaseous state the affinity of unlike atoms for each other becomes the stronger force. At still higher temperatures, even these forces are overcome by the repulsive action of heat. We may say that heat overpowers the forces of aggregation (like with like) first, and those of chemical affinity (like with unlike) later and with more difficulty. Now mercury at 800° has reached this latter stage, and it is claimed that argon at ordinary temperatures is in the same condition.

The analogies of argon are evidently with such elements as H, N, O, F, and Cl, that is to say with the metalloids of low atomic weight and specific gravity, gaseous at ordinary temperatures, somewhat soluble in water, with very low melting and boiling points, and very difficult to reduce to the liquid and solid state; rather than with the metals, among which mercury must be grouped, characterized by high atomic weights and specific gravities, liquid or solid at ordinary temperatures, insoluble in water, with much higher melting and boiling points, and easily reduced to the liquid and solid state.

In endeavoring to draw conclusions as to the argon molecule, it would therefore seem less forced to reason from what we know of the former, the metalloids, which it closely resembles, rather than the latter class of bodies, the metals, with which it has but few analogies. We are thus led to regard argon as a body in which the atoms in the molecule (if di- or *n*-atomic) are very firmly bound together, like nitrogen for example, and in fact from whatever side we approach the question we are struck with certain marked analogies existing between these two elements. The inert character of nitrogen and its disinclination for direct combination with other substances, has always been regarded as proving the strength of the force aggregating its atoms into a molecule, rather than showing that the substance is monatomic, and at a temperature so high that it is above or near the point at which combination is no longer possible; and why not also in the case of its analogue, argon?

Of the five gaseous elements to which argon is most closely analogous, H, N, O, F, Cl, all are at all ordinary temperatures far below the point at which combinations with other elements are impossible, and why should it be thought that argon is in any way different from them and above instead of below that temperature?

Let us consider the following table:

Metalloids						Metals	
H	N	O	F	A	Cl	Na	Hg
1	14	16	19	20	35·5	23	20
gas	gas	gas	gas	gas	gas	solid	liqui
colorless	colorless	colorless	greenish	colorless	greenish yellow	white	whi
electro neg.	electro neg.	electro neg.	electro neg.	?	electro neg.	electro pos.	electro
Sp. Gr. ?	·90	1·37	1·265	1·5	1·33	·98	13
M. P.	−214°		below	−189·6	−102°	95·5°	−38
B. P. −243°	−194°	−182·7°	−·95°	−187·	−33·6°	red heat	+357
At Vol	15·5	14·	15·5?	13·3	25·6	23·5	14

Evidently argon has the characteristics of a metalloid rather than of a metal.

Now of these bodies, F, Cl, and O at ordinary temperatures exhibit the strongest tendencies known for combination with other substances, and H and N, in the nascent state, are almost equally endowed with chemical energy, but this energy is masked so to speak, gradationally, by the force holding the atoms together in the molecule which acts against and in opposition to the force tending to cause chemical combination. This opposing force of aggregation, comparatively weak in F, is stronger in Cl and O, still stronger in H, very much stronger in N, and why not also, let us say, even stronger yet in argon; thus accounting for its chemical inertness.

Indeed, is there any good ground, reasoning from the known properties of these elements (if it be an element), for believing argon to be in such a different physical condition from the rest of them, as is implied in the assumption that it is too hot to combine with other elements?

The discoverers in their memoir have remarked, that "the chemical behavior of nitrogen is such as to suggest that its dissociated atoms would possess a high degree of activity, and that even though they might be formed in the first instance their life would probably be short." Could not this language with great propriety be applied to its analogue, argon, also?

The theory, upon which argon at ordinary temperatures is considered to be in the same physical condition as mercury at 800°, is probably somewhat as follows: Starting with the elements in the solid state at the absolute zero of temperature, and devoid of energy or tendency towards chemical combination with other bodies, as temperature increases they finally become liquid and then gaseous. The increasing affinity toward other bodies increases with liquefaction, and still more so when the elements are vaporized; finally the heat becomes sufficient to dissociate the molecules into free atoms, in which state the tendency towards chemical combination is at its maximum, because the opposing force of molecular aggregation is reduced to zero. From this point on, an increase in temperature decreases the affinity towards other substances, until finally we arrive at a temperature above which the repulsive

force of heat (if such an expression be permissible), renders all combination impossible; which is the physical condition in which argon, at ordinary temperatures, is by this theory assumed to be.

Chemical affinity, then (the tendency for instance of the molecules H^2 and Cl^2 to form 2HCl), is not a simple force, but rather the resultant of at least three other *atomic*, not molecular, forces, viz: the attraction between the atoms H and Cl, which is opposed by the attractions between H and H and Cl and Cl. In general

$$F = f - \frac{c+h}{2}$$

where F = the chemical affinity of chlorine for hydrogen
f = the attraction between the atoms H and Cl
c = " " " Cl " Cl
h = " " " H " H

The theory assumes f, c and h to decrease with a rise, and increase with a fall in temperature, but f more slowly than c and h. When $f = \frac{c+h}{2}$, F = 0. If temperature be reduced f increases more slowly than $\frac{c+h}{2}$, hence the forces of molecular aggregation c and h are stronger the lower the temperature, while F, the affinity for other molecules, has a negative value.

Per contra, if temperature be increased, f decreases more slowly than $\frac{c+h}{2}$, and when $\frac{c}{2} + \frac{h}{2} = 0$, f will have a positive value, and F will have its maximum value, that is $F = f$; the case corresponding to the point where heat has dissociated the molecules into nascent atoms. Or rather the maximum value of F will occur somewhere between the dissociation temperatures of Cl and H. When both molecules are dissociated, since $\frac{c}{2} + \frac{h}{2} = 0$, increase of temperature reduces F and where F = 0, which case, for mercury vapor, is reached at 800°, we reach the upper limit of chemical combination; that is, the kinetic energy of the molecule is too great to allow of its combining with other molecules.

The following might at first seem an objection to this theory, viz: that considering the molecule HCl, if temperature is reduced f, the force binding the atoms H and Cl into a molecule finally becomes less than $\frac{h+c}{2}$ hence reduction of temperature ought to produce decomposition of HCl, whereas nothing of the sort occurs.

The answer is this, before HCl can be dissociated into H and Cl so that H^2 and Cl^2 can be formed, we must first overcome the force of attraction between the molecules of HCl,

which, as temperature is reduced, increases until sufficient to unite the molecules into solid HCl. Hence although $\frac{h+c}{2}$ does become greater than f with reduction of temperature, the tendency towards dissociation is more than overcome by the increased force of aggregation between the HCl molecules.

Strictly this molecular force should be taken into account above, but I have omitted it to simplify the discussion. Compare here the following language of Dr. Möller: "Scientists have proved that chemical action entirely ceases even before so low a temperature (−273°) is reached . . . The form of motion which we call affinity between different molecules seems at that temperature to be wholly extinct, but the other form of motion, the affinity between homogeneous molecules and between the atoms of which they are formed, does not appear to be much impaired by the lowest temperature we can produce."*

In general then we may roughly outline the gamut of changes produced by increments of heat energy as follows:

1st. Absolute zero, no energy, maximum of force of aggregation, minimum of force of affinity, solid state.

2d. Liquid state, first marked indications of the force of affinity (though weakly displayed by some solids under great pressures or certain electrical conditions), reduced force of aggregation.

3d. Gaseous state, force of affinity stronger, of aggregation weaker.

4th. Temperature where dissociation begins.

5th. Temperature where dissociation is complete, and the force of aggregation completely overcome as between like atoms. Maximum of chemical affinity in fourth or fifth stage.

6th. Temperature at which the dissociated atom has no affinity for any other atoms, like or unlike.

Let us now consider the following table of melting and boiling points.

	Substance.	Melting Point.	Difference.		Boiling Point.
H^2	= Hydrogen			Metalloids Average difference, 34·3	−243
N^2	= Nitrogen	−214°	19·6°		−194·4
CO	= Carbonic oxide	−207·	17·0		−190·
A^n	= Argon	−189·6	2·6		−187
O^2	= Oxygen				−182
CH^4	= Methane	−185·8	21·8		−164
NO	= Nitric oxide	−167·	13·4		−153·6
Cl^2	= Chlorine	−102·	68·4		− 33·6
Br^2	= Bromine	− 7·2	66 2		+ 59·
I^2	= Iodine	+114	70·		+184
Hg	= Mercury	−38·5	395·5	Metals Average diff., 511·3	+357
Cd	= Cadmium	+320	450·0		+750
Zn	= Zinc	420°	530		abt. 950°
Mg	= Magnesium	abt. 600	large		at very high temperature
Li	= Lithium	180°	670		abt. 750
Na	= Sodium	95·5	large		at red heat
K	= Potassium	60	"		above red heat

* F. P. Möller in Cod Liver Oil and Chemistry, p. 452.

Many of the metals are volatile if at all at such high temperatures that they have not been accurately measured, but generally the difference between the melting and boiling points is very great for metals. Apparently the rule is that the metalloids have a small while the metals have a large difference between their melting and boiling points, that is, that those elements (metals) whose chemical affinity is overcome by a small degree of heat energy, have large differences between their boiling and melting points, but that those (metalloids) whose affinity is only masked by a large degree of heat energy, have small differences between these points.

Thus compare Hg and Cd and the other metals above with H, N, O, Cl, Br and I.

Now if mercury at 800° is devoid of affinity, then the difference between its melting point and boiling point (395°) is about the same as between its boiling point and its upper limit of chemical combination (443°). But in the case of the metalloids, the difference between the melting and boiling points is small 66° to 70° for the halogens, from 17° to 20° for nitrogen, methane and carbonic oxide, and 13·4° for nitric oxide; while in these cases the difference is very large between the boiling points and the upper limits of combination, (by which I mean the temperatures at which chemical affinity is no longer manifest,) and the disproportion between these differences tends to become greater as the element approximates more and more closely to the characters of the ideal metalloid. Thus iodine begins to dissociate at 700° and at 1500° the process is complete, so that the upper limit of combination must be above 1500°, and instead of a ratio of differences like that in mercury of 395° to 443° we should have instead the ratio of 70° to 1416°+. *Inequality of differences characterizes the metalloids, equality the metals.* Now if argon is a metalloid (and is it not one if an element?), ought it not also to have this inequality of differences, and to have its upper limit of combination at a very high rather than low temperature? But if this limit be very high, argon can not at ordinary temperatures be like mercury at 800°, that is too hot to combine with other elements.

Again, if, as is the case, the melting and boiling points of argon are very close to each other, ought we not to expect that its melting point and upper limit should be separated by an interval correspondingly great?

In Br and Cl the characteristics become less metallic than with I, and approach more nearly to those of the ideal metalloid; and we find that while the difference between the melting and boiling points is but little changed, the differences between the boiling points and the upper limits are very greatly

increased. The same is equally true of N, O and H. Why not also of argon? The characteristics of argon are preëminently non-metallic, the difference (2·6°) between its melting and boiling points is small, as it should be, and not large as in the case of metallic mercury (395·5°); hence the inference that like other metalloids its upper limit of combination is far removed from its boiling point, much farther so than in the case of mercury, that is, far above 800°. But we are asked to believe that it is even below the ordinary temperature of the laboratory. Everything, however, seems to me to point to the contrary conclusion, that argon, like hydrogen, nitrogen, oxygen, chlorine, bromine and the other non-metallic elements of its class, has a very high upper limit of combination, and not a low one like the metals; and hence that at ordinary temperatures it is no more above that limit than are oxygen and nitrogen, but that its chemical inertness is fully explained by assuming that the force binding together the atoms within the molecule is strong as in the case of nitrogen (and to a less degree in hydrogen), and that the contrary view is not justified by known facts.

And this brings us back to our starting point. If the inert character of argon is not due to heat, then how can it be monatomic and also devoid of affinity?

To quote from my previous article—"which is the more unique, a diatomic gas without rotational energy, or a free atom devoid of chemical affinity?" The presumption is at once strongly raised that it is not a monatomic gas but diatomic and chemically inert because the two atoms of the molecule are very strongly bound together, in fact too strongly for any ordinary chemical affinity to overcome the bond, and that perhaps after all there is some hitherto unsuspected weak link in the chain of reasoning supposed to prove its monatomicity, or, as was stated in the editorial in Nature (Feb. 7, 1895): "Till further evidence is forthcoming, a heavy strain is thrown on the link of the chain of argument which connects the ratio of the specific heats with the monatomicity of the gas." I have already pointed out that the conclusion as to monatomicity depends on the correctness of various assumptions which have already been called in question, viz: 1st, that when the rotational energy is small the gas must necessarily be monatomic; 2d, that the ratio of the two specific heats of 1·67 proves absence of rotational energy, and hence monatomicity, and 3d, that the method used for determining this ratio can give correct results. If any one of these propositions fails, monatomicity can hardly be sustained; and any evidence against monatomicity, like that we have been considering, even though not conclusive of itself, yet when construed with these three pro-

positions, already called in question, and with due consideration of the requirements of the periodic law, makes out a pretty strong case, to say the least; and yet even here the future may give us new facts and require us to modify our conclusions; and there is hardly one of the many who have written upon this question that feels like laying down the law dogmatically at the present time, certainly not myself.

Since the publication of my previous paper, a notable discovery, that of helium, has been made by Prof. Ramsay, and the new gas has turned out to be a body very closely analogous to argon. As noted by the discoverer, both bodies resist sparking with O in presence of caustic alkali, both are unaltered by red hot magnesium. In each case the velocity of sound in the gas indicates approximately the value 1·66 as the ratio of the two specific heats, and although opinion is divided, says Prof. Ramsay and his colleagues, on the precise significance of this ratio, it appears to be most probable that in all cases, as in that of mercury, it points to the monatomicity of the molecule.

In general, they say,* an increase in molecular weight is accompanied by a rise in the boiling point, whether in the case of compounds or of elements; and they argue that if argon possessed the atomic weight 20 and molecular weight 40 it is probable its boiling point would lie above that of chlorine instead of being −187° and below that of oxygen, as is actually the case. And this they consider points towards a molecular formula A^1 rather than A^2 and so corroborates the monatomic theory.

It would seem to me, however, as if this conclusion did not follow so plainly as assumed. I have thrown the data upon which the argument is based into tabular form:

Molecule	H^2	N^2	O^2	A^n	O^3	Cl^2	Br^2	I^2
Molecular weight,	2	28	32	40	48	71	158	254
Boiling point,	−243°·5	−194·4°	−182·7°	−187·0	−106°	−33·6°	+59°	+184°
Melting point,	?	−214°	?	−189·6	?	−102°	−7·2°	+114

Now whatever its atomic weight, the molecular weight of argon gas is 40, and if we argue anything at all from molecular weights we shall, I think, be led to place argon in the above table ($A^n = 40$) between $O^2 = 32$ and $O^3 = 48$, into which place its melting and boiling points (respectively −189·6° and −187·°) cause it to fit fairly well. True its boiling point is a little lower, about 4°, than oxygen, while apparently it should be higher. Perhaps later determinations of these points may clear up the anomaly, which is hardly greater than the limits of possible error (in certain directions), or perhaps oxygen, as indicated by the researches of Baly,† may turn out to be a compound and

* Journal Chem. Society, July, 1895.
† Chemical News, April 5, 1895, p. 169.

not a single element, as has been so long supposed; or argon may be a mixture. At any rate, if boiling point is to be raised by an increase in molecular weight I see no reason for expecting $A^2 = 40$ to have a higher boiling point than $Cl^2 = 71$; as the molecular weight is lower so also should be the boiling point, and to my mind the facts either prove nothing or else favor rather than oppose the diatomic theory. If the boiling point depends upon molecular rather than atomic weight, can the boiling point give us any help in determining the atomic weight and the number of atoms in the molecule?

Some additional light seems to be thrown upon the subject by the recently determined refraction equivalent of argon. Mr. R. M. Deeley,* in his paper on this subject, after showing "that the refraction equivalents of the elements vary periodically with much regularity," remarks as follows:

"If argon, like calcium, has an atomic weight of 40, we should expect its refraction equivalent to be also about 10. On the other hand, if its atomic weight be 20, and if it (argon) falls between fluorine and sodium, the refraction equivalent might be 3 or even smaller than that of fluorine (1·6), for between carbon (5 or 6) and aluminum (7·7) the refraction equivalents decrease rapidly until fluorine is reached. They then increase with increasing atomic weight, and more than regain their original value at aluminum. The refraction equivalent is calculated from $P \times \frac{\mu-1}{d}$" (P = atomic weight, d = density, water taken as unity.)

Now Lord Rayleigh† has recently shown that for argon $\mu = 1{\cdot}000281$. This value is certainly remarkable, and proves argon to be as anomalous in its action upon the waves of light as in its behavior as to specific heats. In spite of its greater density (about 1·38, air = 1·) its refraction is only ·961 that of air; whereas, refraction usually increases with the density of the refracting medium instead of decreasing.

If $A^1 = 40$ the refraction equivalent by the above formula becomes about 6·3 instead of 10, the value which Mr. Deeley says would be required, were it monatomic with an atomic weight of 40; but if $A^2 = 40$ whence $A = 20$ (the diatomic theory) the corresponding value of the refraction equivalent 3·14 is entirely consistent with the position of argon in Mendelèeff's classification in Group VIII between fluorine = 1·6 and sodium = 4·3, 3·14 being very nearly a mean between these values; and as Mr. Deeley remarks (l. c.) "the equivalents decrease rapidly until fluorine is reached, and then increase with increasing atomic weight."

* See Chem. News, Feb. 8, 1895, p. 75.
† Nature, July 25, page 293.

The refraction equivalent of nitrogen as given by Mr. Deeley is 4·1 and on the theory (which has many who seem to favor it) that argon is an allotropic form of nitrogen with formula N^3, the corresponding value of the equivalent would be about 2·2 as against 4·1 required, so that this theory does not seem to be sustained. Assuming that the ratio 1·65 has been correctly determined, notwithstanding the criticism of Dr. Stoney, then the anomalous value of the rotational energy (disregarding the questions raised by Col. Basevi) seems to be associated in argon with an equally anomalous value of its refraction equivalent, and the question at once arises whether there is any connection between them.

Nature (July 18, 1895, p. 278), in discussing Mr. C. J. Reed's classification of the elements, makes a somewhat plausible suggestion worthy of consideration should the theory of monatomicity be sustained. "It is remarkable," says the editor, "that if helium has the atomic weight 4 it falls naturally in this group" (viz: $\frac{He}{4}$ 16 $\frac{?}{20}$ 16 $\frac{A}{36}$ 20 $\frac{Fe}{56}$ 28 $\frac{2}{84}$ 20 $\frac{Ro}{104}$ 28 $\frac{?}{132}$, all of which elements, if existent, can be classed as belonging in Family VIII), "and that its atomic weight deduced from the observed density, is somewhat greater than this number. If this difference should be due to the presence of some small quantity of element 84, then the spectroscopic evidence leading to the conclusion that argon and helium contain a common constituent would be explained." This theory assumes the monatomicity of both gases but places A = 36 between Cl = 35·5 and K = 39, which position is in no way inconsistent with the periodic law.

Thus density of helium = 2·13 and ×2 = 4·26 instead of 4.
" " argon = 19·9 and ×2 = 39·8 " 36.

The excessive densities being due to presence of the heavier element 84.*

I also have worked for some years on a classification of the elements, but like many others who have worked along similar lines I have been withheld from publication owing to the uncertainty surrounding the atomic weight determinations, the evidences that there were yet many undiscovered elements unknown to science, and the feeling that in such work, where the tendency to stray away into mere numerical speculation was very great, and where error was so likely to occur from the use of unreliable and imperfect data, the time was not yet fully ripe, and that the case was one where it was best to make haste very slowly.

* That helium is a mixture of several gases is now pretty well settled, and there is some evidence that argon is a mixture also, but not as conclusive.

We seem now, however, to be approaching an era of greater light, and I fully believe that the next few years will be productive of great advances in chemical and physical knowledge. I cannot now go into the subject of classification, but I will in conclusion refer to a closely related subject. In my previous article it will be remembered I called attention to a very regular alternation of intervals of 3 and 1 in the natural series of the elements, and in the table at page 416 of the May number of this Journal will be found a number of terms of the series so formed, not corresponding to known elements, which may possibly represent elements as yet unknown. It is remarkable that so many of those who have been giving their attention to the intricate subject of chemical classification have, by entirely different processes of reasoning, arrived independently at the common conclusion; that there are still a number of undiscovered elements, particularly in what may be termed the eighth or transitional family of Mendelèeff; and furthermore that they have so closely agreed on the atomic weights of the same. Of the various classifications thus far cited in connection with the discoveries of argon and helium, perhaps the most mature are those of Mr. C. J. Reed and M. Lecoq de Boisbaudran. When several investigators, working thus independently, and from data which though at times overlapping so to speak, yet are in the main different, or at any rate lead to different theories and systems of classification; when I say, in such cases, practically the same conclusions are arrived at, these results should naturally command a respectful consideration; and that is precisely what seems to have happened in the present case.

I can bring this out most clearly, I think, in tabular form, comparing some of the terms of the series referred to with the elements predicted by other classifications, etc.

1		2	3	4	5	6	7	8	9
Edwin A. Hill.		Lecoq. de Boisbaudran and B. Brauner.	C. J. Reed.	Dr. J. H. Gladstone.	Lt. Col. Sedgewick.	R. M. Deeley.	Prof. J. Emerson Reynolds.	Prof. Ramsay and colleagues.	Julius Thomsen.
? =	3	2·9							
helium ? =	4	3·9	4		5	5		4·26	4
argon =	20	20·0945	20	20	20	20	20		20
? =	36	36·40 ± ·08	36		37	36	36 to 39	A=40 ?	36
? =	67		68		62				
? =	83	84·01 ± ·20	84		82	83		82	84
? =	116		116				*Note A*		
? =	131	132·71 ± ·15	132		129–130				132

Authorities.

1. Argon, Prouts' Hypothesis and the Periodic Law, this Journal, May, 1895, p. 416.
2. Chemical News, March 8, 1895, p. 116, and June 7, 1895, p. 271, and Jour. Chem. Soc., July, 1895, cccxcii, p. 550.
3. Ibid., May 3, 1895, p. 213; Journal of the Franklin Institute, July, 1895, p. 68, and Nature, July 18, 1895, p. 278.
4. Nature, Feb. 21, 1895, p. 389.
5. Chemical News, March 22, 1895, p. 139.
6. Ibid., May 17, 1895, p. 244.
7. Nature, March 21, 1895, p. 486.
8. Journal Chemical Society, July, 1895, p. 707.
9. Zeit. Anorg. Chemie, viii, 283-8, and Chemisches Central-Blatt, Band II, 1895, p. 429.

Note A. Prof. Reynolds, while indicating the existence of members of Family VIII of higher weight than 36–39, does not assign their atomic weights in the article quoted. Atomic weights are given in the body of the table and the agreement, it will be seen, is very striking. It will be noted that three of the values in Mr. Reed's classification (68, 84, and 132) are just one unit greater than the corresponding values in my own series (67, 83 and 131).

The coincidences are certainly very striking.

New Haven, Ct., Aug. 10, 1895.

Addendum, October 7th, 1895.

The publication of the foregoing article having been delayed until the November issue renders necessary some additional remarks.

Prof. Ramsay (Chem. News, Aug. 2, 1895, p. 51) has produced a compound of carbon and argon by the action of an incandescent carbon arc in an atmosphere of argon. Four hours' action increased the volume one-fifth. Mr. Crookes (Chem. News, Aug. 30, 1895, p. 99) examined the product spectroscopically, finding residual argon, and also a compound with a spectrum very analogous to that of cyanogen and other carbon compounds. This, however, he says, is not evidence favoring the N^3 theory, since most volatile carbon compounds have similar spectra.

In view of the many analogies between argon and nitrogen, this new compound may have the formula CA, and be analogous to cyanogen, which can be formed in a very similar manner; i. e., by passing induction sparks between carbon poles in an atmosphere of nitrogen. This new compound furnishes a strong argument against the theory that argon at ordinary temperatures is like mercury at 800°, too hot to combine (hence its inertness). All the argon compounds thus far formed, as those of Berthelot with benzene and carbon disulphide, and the apparent absorption of argon by the magnesium and platinum poles, have been produced by heating and not cooling argon, and by increasing, not decreasing, its store of energy.

Lord Rayleigh, in his lecture before the Royal Institution (Nature, lii, 159–164) refers to the tendency of ozone O^3 to go slowly back to O^2, the normal type. But Bedson and Shaw (Chem. News, July 26, 1895, p. 48) have shown that the nitrogen contained in the natural crystals of rock salt contains the same proportion of argon as does atmospheric nitrogen, so that in a period of perhaps thousands of years there has been no tendency for argon to become N^2, hence the inference that argon is not N^3. Schild has pointed out (Chem. News, May 31, 1894, p. 259) that if argon is N^3, then any argon compound, when decomposed, should yield nitrogen, the normal, instead of argon, the allotropic form. Now Berthelot has shown (Chem. News, July 5, 1895, p. 1) that the analysis of the resinous compound of argon and carbon disulphide yields argon, not nitrogen, which makes strongly against the N^3 theory.

In line with this are the experiments of Peratoner and Oddo, mentioned by Meldola (Pres. Address, Nature Sept. 12, 1893, p. 483). They recently obtained nitrogen, not argon, from the electrolysis of hydrazoic acid and its salts, and they conclude that an allotropic form of nitrogen is impossible.

Is argon a mixture?

Evidence grows stronger that it is; as to helium there is not much doubt, and if anything can be argued from the analogies between argon and helium, argon is a mixture likewise.

Says Prof. Ramsay (Nature, July 25, 1895, p. 333): At least two helium lines are coincident with one each of two pairs of characteristic argon lines, but not with equal brilliancy, a faint argon line being identical with a prominent red helium line, and a strong red argon line with a faint red helium line; and besides these two there is a line in the orange red, faint in helium, but moderately strong in argon, which is very close if not identical.

Kayser's recent measurements of the argon lines (Chem. News, Aug. 30, p. 99), though measured to one more decimal place, do not agree with those of Crookes. They may not be to the same scale, but Mr. Crookes found 26 lines common to both the red and the blue argon spectra, whereas Kayser states they have no lines in common so far as he can see. This seems to favor the view that the red and blue argon spectra denote different constituents in the gas.

Helium proves much more insoluble in water than argon (1 vol. of water dissolves only ·0073 of helium). It has been found by Kayser associated with argon in the gases of certain mineral springs in Germany, and has also been by him detected in the atmosphere. (Chem News, Aug. 23, 1895, p. 89.) Also by Ch. Bouchard, associated with argon and some other

unknown gas in the gases of certain mineral springs in the Pyrenees mountains (Nature, Sept. 12, 1895, p, 487). The question raised as to the presence in cleveite gas of helium, the element giving the solar line D^3, has now been fully settled, the line being double both in solar and terrestrial helium. A good account of this question and its solution will be found in the Observatory for Aug. 1895, p. 295.

The work of Runge and Paschen upon the spectrum of cleveite gas subdivides the lines into two series, each of which in all probability stands for a different gas or class of gases. They also note certain rythmical relations between the wave lengths and those of hydrogen lines, and note a marked similarity in type between the helium lines and those of the spectra of the alkali metals. (Philosophical Magazine, Sept. 1895, p. 297.)

We come finally to the work of Mr. Crookes on the helium spectrum published in the last issue of the Journal, which may be summarized as follows, the grouping being my own:

HELIUM LINES OBSERVED BY WM. CROOKES, F.R.S., ETC.

Groups.	No. of Lines.	Intensities.			Occurrence in				
		Maximum.	Minimum.	Average.	Uraninite R.	Cleveite R.	Bröggerite R.	Bröggerite L.	Helium Puris.
A	16	30	4	9·2	strong	strong	strong	strong	strong
B	2	10	6	8	strong	strong		strong	strong
C	1	7	7	7	faint	strong		strong	strong
D	1	10	10	10	very faint	very faint		strong	strong
E	1	7	7	7	strong		strong	strong	strong
F	1	10	10	10		strong	strong		strong
G	1	5	5	5			strong	strong	strong
H	3	9	9	9	prominent	very faint		very faint	
h	1	8	8	8	prominent		very faint	very faint	
I	2	10	9	9·5	strong	strong			
J	1	8	8	8				strong	strong
K	1	4	4	4	strong				strong
L	1	10	10	10	very strong	very faint			
M	21	10	3	7·08	strong				
N	18	9	2	5·33					strong
Total	71				11	8	5	9	10

Blank spaces indicate the absence of lines and the table does not include a number of lines for which Crookes in his table gives no data, as for instance 4931·9 intensity 3, 4544·1 int. 5,

etc. The term strong above means that each line is equally strong in the minerals named; thus in Group B, one of the lines has intensity 8 and the other intensity 10, in all samples of the gas except bröggerite R.

The natural inference is that each of the groups A to N represents one or more distinct gases, except that *h* may after all be identical with H. The line D^3 occurs in Group A. Helium purissimum is apparently one of the most complex, and bröggerite R one of the most simple of the five gases. By construing the work of other observers, as Runge and Paschen, with that of Crookes, these groups may be still further subdivided. Apparently the gases given off by minerals of the uraninite type, which are loosely spoken of as helium while they contain helium, are very complex mixtures of gases of the argon and helium types containing anywhere from 4 or 5 to 11 or more distinct constituents.