This method has been used for some months in the laboratory of the New Jersey Zinc and Iron Co., with very satisfactory results. The following table shows how this compares with the ordinary gravimetric methods.

Material Analyzed.	Zinc Gravimetric.	Zinc Volumetric.	Manganese Gravimetric.	Manganese Volumetric.
N. J. ore	22.05	22.11	7.58	7.38
“ “	26.58	26.48	N. D.	11.98
Brass	5.06	5.12	0.	0.
N. J. ore	22.50	22.47	N. D.	11.55
“ “	30.75	30.82	“	7.54
Blende	38.28	38.18	“	0.14
Willemite	55.55	55.68	0.	0.
Residuum	4.60	4.79	12.23	12.30
“	4.29	4.44	N. D.	11.99
“	9.15	8.99	“	11.61
Tailings	2.12	2.05	6.04	6.00
Middles	15.15	15.24	9.24	9.14

In conclusion I wish to express my thanks to Mr. D. A. Van Ingen, who has done much of the experimental work necessary in testing the method.

SOME PHYSICAL ASPECTS OF THE NEW GAS, ARGON. THE IDEAL THERMOMETRICAL SUBSTANCE FOR HIGH TEMPERATURES.

BY W. R. QUINAN.

Received March 31, 1895.

THE discovery, by Lord Rayleigh and Professor Ramsay, of a new gaseous constituent of the atmosphere, has a many-sided bearing upon science and excites the interest of the whole world.

While there may be mooted questions yet to be decided in regard to the elementary constitution of argon, certain extraordinary conclusions seem to have been reached. In the sense of the kinetic theory, it is a monatomic gas; that is, if heat be applied to it, all or very nearly all of this heat will be expended in dynamic energy. The kinetic theory, whatever may be its shortcomings, is certainly the most intelligible hypothesis now at our command, both to explain and to expound the ideal behavior of matter in its simplest form—the gaseous. The behavior, it must be remembered, is independent of the theory. It is the fruit of experimental research.

According to the kinetic theory, in a monatomic gas the ratio of the specific heat under constant pressure to the specific heat at constant volume is one and two thirds. In diatomic gases, some of which are sufficiently normal in their behavior at ordinary temperatures to allow the experimental ratio to be taken as the theoretical—this ratio is about 1.41. In triatomic gases the theoretical ratio is 1.273, and so on according to a relation applicable to all molecules except monatomic

$$\gamma = 1 + \frac{0.41}{\frac{1}{2}N}. \quad \text{(a)}$$

in which γ is the ratio and N the number of atoms in the molecule.

The kinetic view is briefly as follows: A gas consists of discrete molecules endowed with energies. Of these, the dynamic energy, referred to the units of space and time, is measured (under the condition of uniform distribution) by the pressure. This is due to the motions of the molecules as entities. But the molecule itself is usually a complex system, consisting of two or more united atoms. The parts of this secondary system are capable of rotation about their center of mass and, perhaps, of various other movements, such as vibrations of the constituent atoms. The energy absorbed by the motions of this secondary system (under the condition of rest for the center of mass) may be called for simplicity the internal energy, while that due to the movement of the molecule as a whole may be called the kinetic. According to the conception and the laws of mechanics, the "free path" of a molecule is rectilinear. By encounters or collisions between the molecules there is a constant exchange and redistribution of the energy between these two forms of energy, but for every gas (in the ideal state) a constant ratio is preserved between the two forms, and each form, therefore, preserves a constant ratio to the whole energy.

In all gases, the ratio β of the whole energy to the kinetic, bears a simple relation to γ, the ratio of the specific heats, as follows:

$$\beta = \frac{2}{3(\gamma - 1)} \quad \text{(b)} \qquad\qquad \gamma = 1 + \frac{2}{3\beta} \quad \text{(c)}$$

Combining (b) with (a) above we have

$$\beta = \frac{N}{1.23} \quad (d)$$

This formula (d) like (a), from which it is derived, applies to all molecules except monatomic.

In a monatomic gas the only energy which can be absorbed by the molecule (single atom), considered at rest with respect to its center of mass, is one of rotation. On account of the infinitesimal size of the atom this energy is negligible, and for such a gas β may be taken as unity; whence, as from formula (c) $\gamma = 1\frac{2}{3}$.

The gases believed to be monatomic by chemists are the vapors of sodium, cadmium, zinc, and mercury. Until the discovery of argon, the only gas for which the relation above had been verified was mercury. Kundt and Warburg showed, by comparing the wave-lengths of the same sound in air and mercury vapor, that γ for the latter was one and two-thirds—an extraordinary confirmation of the bold speculations of Clausius.

Argon has dispelled certain beliefs in regard to monatomic gases. High boiling-points can no longer be regarded as characteristic.

Whatever nomenclature we adopt, whether we accept the ingenious suggestion of Professor Dolbear, in his "Matter, Ether, and Motion," that the internal energy of a gas is to be considered its "heat" proper, or content ourselves with Helmholtz's wider generalization of "free" and "bound" energy, the *fact* is none the less certain, that the energy of gases (monatomic excepted) exists in two distinct forms. In no other simple way can we account for the difference in the action of heat upon them—a difference directly connected in the molecular hypothesis with their complexity of constitution.

The conception of β as well as that of γ is, therefore, founded in fact.

The relations of β and γ are independent of the kinetic conception. To deduce them it is only necessary to supplement the laws of gases with two other laws, both well founded; *viz.*, Avogadro's, that equal volumes of gases under like pressure and temperature contain equal numbers of molecules, and the hypothesis of Clausius that the specific heat of an atom in the (perfect) gaseous state is constant and the same for all elements. This latter hypothesis is the corner-stone of the kinetic theory in which Avogadro's law, as well as the laws of gases, is a rigid deduction.

The theoretical behavior of gases under changes of temperature, pressure, and volume, is regulated by the law of Boyle and the law of Charles. According to the first, at constant temperature the product of the pressure and volume is constant; according to the second, equal volumes of all gases expand equally under constant pressure, or show equal increments of tension at constant volume, for equal increments of temperature.

These laws are ideal. No gas obeys them with perfect accuracy under every condition, nor even with approximate accuracy under certain conditions. Nevertheless, they have a reality. Any one familiar with the mathematical theory of "limits" can understand their relation to the behavior of gases. We arrive at the conception of the *perfect gaseous state* in the following simple way:

If we trace the properties of a gaseous substance through a considerable range of temperature, we find that below a certain temperature, even under atmospheric pressure, the substance is a liquid. This is its boiling-point. Above this, for a certain range of temperature, although gaseous under ordinary conditions, it may be condensed into a liquid by increasing the pressure, till at length we reach a temperature above which this is impossible. This is its critical or absolute boiling-point. Above this temperature the substance is a permanent gas, but near it the gas is notably "imperfect." As we raise the temperature above this point the behavior becomes more and more nearly normal. The ideal state for every gas is, therefore, simply a question of its state of removal from the critical temperature.

MEASUREMENTS OF HIGH TEMPERATURES.

Temperature is the intensity factor of heat—the thermal form of energy. It is practically measured by the voluminal expansion of a standard substance. In the thermodynamic theory, it is independent of the properties of any particular substance. The absolute values of two temperatures, one higher than the other, are to each other as the heat taken in, to the heat rejected by a perfect thermodynamic engine (with reversible cycle) working between the two temperatures as limits. The value of the degrees being fixed, this scale of temperature agrees very closely with the scale determined by the air-thermometer. It agrees perfectly with the ideal scale of perfect gases, in which equal increments of temperature correspond to equal increments of heat (mass being constant)—a principle simply expressed by saying that the specific heats are constant.

So far in science the attempts at accurate measures of high temperatures have been indissolubly connected with the increase of volume or tension of elementary gases, such as hydrogen and nitrogen. The regularity of their behavior under ordinary conditions of pressure and temperature has been checked and confirmed in various ways. Since the general effect of increasing the temperature is to correct and improve the isothermals of gases, it has been assumed that this regularity is sustained at high temperatures.

These gases have, however, a fatal theoretical defect when used as thermometrical substances at very high temperatures. Being diatomic a certain part of their energy (about 38.5 per cent.) takes the form of internal energy. This is the form in which we believe the heat exerts its decomposing influence. However this may be, these gases are theoretically subject to a gradual thermolysis or decomposition by heat. A part of the heat being rendered latent and being without effect upon the temperature, equal quantities of heat cease to correspond to equal degrees of temperature. Moreover, since in this dissociation of the molecule the specific volume is doubled, the coefficient of expansion under constant pressure or the coefficient of tension at constant volume, is changed, and the scale of temperature based upon either becomes unreliable.

Now, argon, as a thermometric substance at ordinary temperatures, has about the same properties as nitrogen or oxygen. It is a permanent gas with a low critical point—121° C. Its behavior under the usual conditions will be very similar to that of the mixture of nitrogen and oxygen we call air; its scale is therefore strictly comparable with that of the air-thermometer.

At high temperatures it is the ideal thermometric substance.

Neglecting dissociation, all gases improve in their behavior as the temperature rises; all discrepancies pass into the normal[1] which does not affect the scale of temperature of either the constant-volume or constant-pressure thermometer.

Argon has no internal energy; the decomposing influence of the heat is absent; in other words, being monatomic it cannot suffer dissociation and its behavior as a thermometric substance throughout the range of temperature will be strictly normal. No other substance has such simple heat relations over such a great range of temperature.

These theoretical considerations would seem to show that argon has great possibilities for usefulness in the hands of the skilled experimenter. In its discovery science has been given a new instrument of research. If by its use we can detect in the behavior of an elementary diatomic gas at high temperature, such an aberration as would be accounted for by the dissociation of the molecule, this will go far to confirm the conception of discrete molecules, the tenets of modern chemistry, and the kinetic theory of gases. Unless the molecular theory can make new conquests like these, the onward march of science bids fair to overthrow it. Already serious attacks have been made upon it, two of which have appeared in this JOURNAL, *1893*, 430; *1894*, 516—the brilliant papers by Prof. Trevor. While Prof. Trevor does not do the theory justice, in fact treats it very cavalierly; he is not the only thinker of the present day who has turned his back upon it. The necessity of reducing the mysterious thing we call *chemical energy* to the reign of law, has led to this estrangement. This form of energy is so obscure that we can apply to it only the most general laws of energetics. We must suppose it to consist of an intensity and a capacity factor, and to be convertible into other energy forms with a constant quantitive relation. But even these simple postulates involve us in difficulties with the molecular hypothesis. Intensity determines action. In order that two bodies may react chemically

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[1] The normal discrepancy is as follows: All gases are compressed less under great densities and expand more under extreme rarefaction than required by the law of Boyle pv = constant—that is the isothermal is normal except near the extremes of pressure and volume for which the product pv is too large.

they must differ in chemical intensity. But what is chemical action? According to one view, it is a change in which chemical intensities are equalized, with a conversion of part of the chemical energies concerned into other energy forms ; according to the other it is a union of atoms. But how can two things, which we suppose to be exactly alike, unite? Whence comes the difference of intensity? By virtue of what principle is the elementary diatomic molecule formed? If this molecule always preserved its integrity, we could regard its diatomic constitution as an elementary condition, but according to our chemical theories, the molecule in many chemical reactions is subject to division. Nevertheless, whenever the atoms are set free they combine according to the diatomic pattern.

It is thus roughly shown that the later views of chemical energy are not supported by the molecular hypothesis. Which shall we throw overboard for the sake of the other, or may we hope for a view which will embrace, possibly revise, and reconcile both?

THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.[1]

BY FANNY R. M. HITCHCOCK.

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THE estimation of molybdic and tungstic acids, and their separation from each other have been the subject of many investigations, but notwithstanding the time and care expended the results so far attained are not perfectly satisfactory, particularly as regards their separation. The reactions which take place when either element is tested alone cannot be depended upon when the two are together, each seeming to exert some modifying action on the other.

Several years ago, Smith and Bradbury[2] carried out a series of experiments on the precipitation of these two acids, chiefly with salts of the heavy metals. Their research brought out many new and interesting facts relating to the precipitation and

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[1] From the author's thesis presented to the Faculty of Philosophy of the University of Penn'a for the degree of Doctor of Philosophy. *1894*.

[2] *J. Anal. Appl. Chem.*, September. *1891*.