XXV. *On the Changes of Temperature consequent on any Change in the Density of elastic Fluids, considered especially with reference to Steam.* By Mr. THOMAS WEBSTER, M.A. of Trinity College, Cambridge. Communicated by Mr. JAMES SIMPSON, M.Inst.C.E.

MY attention having been for some time directed to the theory and constitution of fluids; it has appeared to me that there are some properties of which little notice has been taken, but which, being of considerable practical importance, ought to receive the attentive consideration of scientific men, and especially of those who possess the opportunities of deciding on their value. On the present occasion I beg to offer a few observations respecting these properties. I wish, then, to call attention to the *change of temperature* which always accompanies a *change in the density* of an elastic fluid, and to the consequent change in the elastic force due simply to that change in temperature, as distinguished from the change which is due to the change of density according to the law of Boyle. It has long been observed, that the sudden compression of any quantity of common air is attended with a great degree of heat, and its sudden expansion with a great degree of cold. Thus, if a piston, having a small piece of tinder attached to it, be pressed suddenly down in a cylinder of air or gas, the heat evolved, or squeezed out, by the compression will ignite the tinder; and again, if a delicate thermometer be placed under the receiver of an air-pump, it will indicate cold produced on every stroke of the pump. These effects will not continue long, since there will be an immediate transfer of heat, according to the well known laws of the radiation of heat; thus the heat evolved by the condensation will be rapidly lost among, and that absorbed by the expansion will be supplied from, the surrounding bodies, the general fact being, that the temperature always tends rapidly to equilibrium. The beautiful and simple apparatus of Gay-Lussac may be mentioned, since it exhibits at once both the phenomena in question. Let two spherical glass vessels communicate with each other by a stop-cock, and have a delicate thermometer suspended at their centres; then if one have the air exhausted, and the other be filled by a condenser, either with common air or with a gas, and the stop-cock be opened so that the condensed air rushes into the empty vessel, the thermometer in one vessel will sink and in the other will rise; namely, it will sink in that which is being emptied, or in which the air is expanding, and it will rise in that which is filling, or in which the air is being condensed; and when the experiment is

made with great care, it will be seen that the cold indicated by one corresponds exactly to the heat indicated by the other. If another thermometer be suspended in the empty vessel close by the orifice, that is, just where the air is in the act of expanding, a very great degree of cold will be indicated; and this will diminish rapidly as it is placed further from the orifice. These indications of heat and cold continue but for a very short period, since the equilibrium of temperature is almost instantaneously restored. No accurate measure of the heat absorbed and developed can be procured by direct observations on the thermometer; it may, however, be calculated from the change in the elastic force, as we shall see presently. This experiment of Gay-Lussac does not appear to have been repeated on a large scale; but I conceive that if a large cylinder of thin metal were placed in communication with a vessel of condensed air at a great pressure, the cold produced at the one end, where the expansion was proceeding, and the heat produced at the other, where the condensation was taking place, would be quite sensible to the hand, and a series of air-thermometers would indicate very different states of temperature at the same distances from each end. But the important practical inquiry is the change which this developement and absorption of heat produces on the elastic force of the fluid; there must be increase of elastic force due to this increase of temperature, and a diminution of elastic force due to the diminution of temperature, besides the increase and diminution which is due to the change of density according to Boyle's law. In fact, we know that Boyle's law is not true, unless the compressed air is allowed time to cool, as was distinctly ascertained in the series of experiments made by order of the Academy of Paris on this subject. In the complete investigation of it by Desormes and Clements, which I have detailed at full length in my *Theory of Fluids*, Article 98, the increment of temperature is calculated by a series of mathematical reasoning, from this very change in the elastic force for which I contend. The problem proposed was "to determine the increment of temperature for a given small condensation." They observed the successive changes which the mercurial column underwent when air was first let into an exhausted receiver, and after it had lost the small increase of temperature due to the small condensation. The column always sunk by a small quantity, and the amount of this change enabled them to determine the amount of heat developed for a given condensation. Of the accuracy of their results there cannot be the least doubt, for two other and quite independent phenomena, in which

the same causes are called into operation, namely, the production of sound and the vibration of a cylindrical column of air, give results according with very great accuracy. The preceding facts are mentioned, to give confidence in the principle for which I contend, that whenever there is a change in elastic force according to the law of Boyle due to the density, there is also an additional change in the elastic force due to the change of temperature, which is the necessary consequence of this change in the density: for it must be remembered, that in all the experiments, the elastic force agrees with the law of Boyle so soon as the equilibrium of temperature is restored.

On this part of the subject it is unnecessary to insist, since the facts are well established for most of the elastic fluids, but the experiments, so far as I have become acquainted with them, do not extend to steam, and unless there be some reason for excluding steam from the general properties of all other elastic fluids, we must admit the preceding conclusions with respect to it also. Now so far from having any reason to except steam from these laws, we have every reason for believing that steam separated from its water, and maintained at a higher temperature than 212° , differs in no respect from the permanent gases. It can be readily liquified, but doubtlessly all the gases can be reduced to the same form by a proper increase of pressure and diminution of temperature.

For if we consider steam as an elastic fluid owing its elastic qualities solely to the repulsive power of heat, there can be no reason *à priori* for excepting it from the laws of other elastic fluids, which appear to owe their energy and existence to the same cause. Now so far as experiments have been made, it appears that steam expands equally for all equal increments of temperature; thus following the law of other elastic fluids. There is a passage in Professor Robison's Treatise on Steam which involves the principle in question, but which appears not to have been followed out. He says, "it is well known that when air is suddenly expanded, cold is produced, and heat when it is suddenly compressed. When making experiments with the hopes of discovering the connexion between the elasticity and density of the vapours of boiling water and also of boiling spirits of turpentine, we found the change of density accompanied by a change of temperature vastly greater than in the case of incoercible gases. When the vapour of boiling water was suddenly allowed to expand into five times its bulk, we observed the depression of a large and sensible thermometer to be at least four or five

“times greater than in a similar expansion of common air at the same temperature.”

The fact of the depression being greater in the expansion of steam than of air at the same temperature, is explicable at once from the different constitutions of the two fluids with respect to the properties of heat; but on this I cannot at present enter. The fact is invaluable as coming from such a man, and, when viewed in connexion with the general theory of elastic fluids, and the above-mentioned law of Gay-Lussac respecting the expansion of steam for increments of temperature, entitles us to assume that, so long as steam retains its gaseous character, it is subject to the laws of gases. These conclusions might be sustained by many well known phenomena respecting vapours and evaporation generally, but enough has been said to warrant our including steam in the general law of the French philosophers respecting elastic fluids: “That equal volumes of all elastic fluids, taken at the same temperature and the same pressure, being suddenly compressed or expanded by the same fraction of their volume, disengage or absorb the same absolute quantity of heat.”

Now the degree of heat or cold produced depends on the rate at which the change takes place; and this consideration will lead to some important conclusions with respect to the expansion of high-pressure steam. The rate of expansion will obviously depend on the elastic force of the steam; the higher pressure therefore which we use the greater will be the cold and the greater the diminution of the elastic force beyond that which the law of Boyle would give. Suppose steam of ten atmospheres suddenly to expand to four times its bulk, then the elastic force of the expanded steam ought, on these principles, to be much less than the elastic force of steam of five atmospheres suddenly expanded to twice its bulk; and the greater the elastic force of the steam, the greater will be the deviation from the law of Boyle. So that, while Boyle's law will be nearly true for steam of one or two atmospheres, it will be most untrue for steam of five or ten atmospheres. These, I conceive, are results which may be readily tested by careful experiments. I know of none in which they have been fairly examined, for I am not willing to admit the conclusions which may be drawn from some accounts of steam worked expansively, and which would appear to militate against these principles; but on this I shall say more immediately.

It would appear then, that the mere rate of expansion may be such, that

the diminution of elastic force, consequent on the diminution of temperature, may leave scarcely any elastic force in the expanded steam; so that there may be extreme cases in which the law of Boyle will appear absolutely false. These conclusions appear to me supported and illustrated by the facts, that high pressure steam does not scald, and that elastic steam is not so efficacious as gunpowder for throwing bullets or other masses.

When low pressure steam expands into the air, it preserves very nearly both its density and its temperature, but when steam of a high pressure expands, the instantaneous augmentation of volume demands that a large portion of heat should become latent, or it cannot exist at all as steam. If the expansion were to stop the instant at which the elastic force of the steam becomes equal to that of the atmosphere, its temperature would (since the sum of the sensible and latent heat is invariable) descend only to 212° ; but in consequence of the momentum which the particles have acquired from the rapidity of the expansion, it expands far beyond this limit, so that the diminution of temperature becomes greater, in proportion as its original elastic force was greater than the elastic force of the atmosphere. If this expansion takes place in a vacuum, the reduction of temperature will be greater still, since the particles of air present mechanical obstacles to the expansion. So that in some cases the elastic force may be lost almost entirely. We know, thanks to the ingenuity of Mr. Perkins, that highly elastic steam will impel bullets with considerable velocity; this velocity does not, however, appear to be equal to that which can be generated by gunpowder. Now in order to increase the velocity, we must increase the elastic force of the steam, the consequence of which being an increased rapidity of expansion, the additional reduction of temperature may more than nullify the original increase of elastic force, so that steam at a higher pressure will be less efficacious than steam of a less pressure. If this be the case, there is some temperature at which for a given ball the effect is a maximum, that is, greater than either at a higher or a lower temperature. But in the case of gunpowder the temperature of the elastic fluid is kept up by the continued consumption of fresh materials; the heat evolved during the combustion of these ingredients is quite prodigious, so that we have, in fact, the repulsive power of heat itself in full agency. I have said nothing respecting the density of the steam at different temperatures, my object not being to discuss this question fully, but merely to illustrate what must, I conceive, be the necessary consequence of increasing the temperature and elasticity of the steam beyond certain limits.

The application of these principles to the working of *steam expansively* is at once apparent ; there will in every case be a diminution in the pressure exerted beyond what will be given by Boyle's law, and this will be greater the more rapidly the engine is worked. But on this subject I hardly dare venture any remarks ; practical considerations are of much greater value than any which I can offer, especially as in one large class of engines, namely, in condensing engines, where the steam is worked at a low pressure, the deviations from the Boylean law, due to the cause which I have mentioned, cannot be considerable ; still, however, these deviations must, I conceive, be appreciable whenever the steam is generated at a higher temperature than 212° . But in high pressure engines the deviations due to this cause must be considerable, and I would venture to suggest that if higher pressure steam be used than is from the circumstances of the case practically necessary, the steam generated is not applied in the most economical manner, so far as concerns the ratio of the work done to the fuel consumed. The preceding remarks have referred exclusively to steam separated from its water and maintained at such a temperature that it may be considered as a permanent gas. If the steam be not separated from its water, the case is so entirely different, that the preceding remarks do not at all apply.

If the space above the water be not saturated with vapour, that is, if the vapour which it contains have not the maximum density due to the temperature of the water, it is owing to the mechanical obstruction of the particles of air ; but since we suppose the air removed, or the space full of steam, we have to consider the nature of the changes which take place when this given space is increased or diminished, that is, when the pressure on the surface of the water is diminished or increased. In this case the law of Boyle has no existence, for it applies only to a permanent gas, that is, it is only a steam law, when the vapour is detached from its liquid and contained in a space of such a temperature that it may be considered as a permanent gas. The pressure of the existing vapour on the surface of the water being the only limit to the formation of fresh vapour, whenever the pressure on this surface is diminished in the boiler by the withdrawal of a portion of the steam, fresh steam will instantly be formed, so that if, where steam is worked expansively, there be any water at the bottom of the cylinder, or any communication whatever with any water, the effect will be precisely the same as if the communication with the boiler were not entirely cut off ; there will be a constant accession of steam, or fresh steam will be formed as fast as

the piston rises. It has sometimes been stated that where steam is worked expansively, the effect is greater than the Boylean law would lead us to suppose; if such appear to be the case, it must be from some such cause as the above mentioned; either the steam is not entirely cut off, or there is some communication with water: the smallest quantity of water will be sufficient to increase very considerably the apparent effect, and cause a great deviation from the calculated elastic force. The whole theory of this subject is so intimately connected with the theory of heat, and the elasticity of the fluid depends so entirely on the repulsive power of heat, that the consequence of its known laws may be immediately traced in every application of steam; hence we may be convinced that there is a loss of elastic force, besides that which is due to the change in density, whenever steam is worked expansively, however much it may be practically overruled and modified. As a means of detecting this I would mention, that it ought to be shewn by the greater supply of heat which a cylinder requires when the steam is worked more expansively, than where the same steam is worked less expansively. From these considerations we may see that there is a maximum in the useful effect of expansion working; but the complete determination of it is a purely practical question, and since it will depend on the conducting power of the metal, it must be somewhat different for every different engine.