Joseph Black (1728-1799)

excerpts on specific heat and latent heat from

Lectures on the Elements of Chemistry delivered in the University of Edinburgh by the Late Joseph Black, M.D. ...

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[Specific Heat]

A second improvement in our knowledge of heat, which has been attained by the use of thermometers, is the more distinct notion we have now than formerly, of the *Distribution* of heat among different bodies.

I remarked formerly, that, even without the help of thermometers, we can perceive a tendency of heat to diffuse itself from any hotter body to the cooler around, until it be distributed among them, in such a manner that none of them are disposed to take any more heat from the rest. The heat is thus brought into a state of equilibrium. This equilibrium is somewhat curious. We find that when all mutual action is ended, a thermometer, applied to any one of the bodies, acquires the same degree of expansion: Therefore the temperature of them all is the same, and the equilibrium is universal. No previous acquaintance with the peculiar reaction of each to heat could have assured us of this, and we owe the discovery entirely to the thermometer. We must therefore adopt, as one of the most general laws of heat, that "all bodies communicating freely with each other, and exposed to no inequality of external action, acquire the same temperature, as indicated by a thermometer." All acquire the temperature of the surrounding medium.

By the use of these instruments we have learned, that if we take 1000, or more, different kinds of matter, such as metals, stones, salts, woods, cork, feathers, wool, water and a variety of other fluids, although they be all at first of different heats, let them be placed together in the same room without a fire, and into which the sun does not shine, the heat will be communicated from the hotter of these bodies to the colder, during some hours perhaps, or the course of a day, at the end of which time, if we apply a thermometer to them all in succession, after the first to which it is applied has reduced the instrument to its own temperature, none of the rest are disposed to increase or diminish the quantity of heat which that first one left in it. This is what has been commonly called an equal heat, or the equality of heat among different bodies; I call it the *equilibrium of heat*. The nature of this equilibrium was not well understood, until I pointed out a method of investigating it. Dr. Boerhaave imagined, that when it obtains, there is an equal quantity of heat in every equal measure of space, however filled up with different bodies; and Professor Muschenbroeck expresses his opinion to the same purpose: "Est enim ignis aequaliter per omnia, non admodum magna, distributus, ita ut in pede cubico auri et aëris et plumarum, par ignis fit quantitas."[1] The reason they give for this opinion is, that to whichever of those bodies the thermometer be applied, it points to the same degree.

But this is taking a very hasty view of the subject. It is confounding the quantity of heat in different bodies with its general strength or intensity, though it is plain that these are two different things, and should always be distinguished, when we are thinking of the distribution of heat.

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It was formerly a common supposition, that the quantities of heat required to increase the heat of different bodies by the same number of degrees, were directly in proportion to the quantity of matter in each; and therefore, when the bodies were of equal size, the quantities of heat were in proportion to their density. But very soon after I began to think on this subject, (anno 1760) I perceived that this opinion was a mistake, and that the quantities of heat which different kinds of matter must receive, to reduce them to an equilibrium with one another, or to raise their temperature by an equal number of degrees, are not in proportion to the quantity of matter in each, but in proportions widely different from this, and for which no general principle or reason can yet be assigned. It will be proper to consult, on this subject, the Comment. de Rebus in Medicina Gestis, vol. 21 and vol. 26, containing the valuable experiments of Jo. Carl. Wilcke, extracted from the Swedish Transactions. Also experiments of Professor Godolin [Gadolin?], in the Nova Acta Reg. Societ. Upsalensis, tom. 5. This opinion was first suggested to me by an experiment described by Dr. Boerhaave (Boerhaave Elementa Chemiae, exp. 20, cor. 11.) After relating the experiment which Fahrenheit made at his desire, by mixing hot and cold water, he also tells us, that Fahrenheit agitated together quicksilver and water unequally heated. From the Doctor's account, it is quite plain, that quicksilver, though it has more than 13 times the density of water, produced less effect in heating or cooling water to which it was applied, than an equal measure of water would have produced. He says expressly, that the quicksilver, whether it was applied hot to cold water, or cold to hot water, never produced more effect in heating or cooling an equal measure of the water than would have been produced by the water equally hot or cold with the quicksilver, and only two-thirds of its bulk. He adds, that it was necessary to take three measures of quicksilver to two of water, in order to produce the same middle temperature that is produced by mixing equal measures of hot and cold water.

To make this plainer by an example in numbers, let us suppose the water to be at the 100th degree of heat, and that an equal measure of warm quicksilver at the 150th degree, is suddenly mixed and agitated with it. We know that the middle temperature between 100 and 150 is 125, and we know that this middle temperature would be produced by mixing the cold water at 100 with an equal measure of warm water at 150; the heat of the warm water being lowered by 25 degrees, while that of the cold is raised just as much. But when warm quicksilver is used in place of warm water, the temperature of the mixture turns out 120 degrees only instead of 125. The quicksilver, therefore, is become less warm by 30 degrees, while the water has become warmer by twenty degrees only; and yet the quantity of heat which the water has gained is the very same quantity which the quicksilver has lost. This shews that the same quantity of the matter of heat has more effect in heating quicksilver than in heating an equal measure of water, and therefore that a smaller *quantity* of it is sufficient for increasing the sensible heat of quicksilver by the same number of degrees. The same thing appears, whatever way we vary the experiment; for, if the water is the warmer mass, and quicksilver the less warm one, by the above difference, the temperature produced is 130. The water, in this case, is become less warm by 20 degrees, while the heat it has lost, being given to the quicksilver, has made this warmer by 30 degrees. And lastly, if we take three measures of quicksilver to two of water, it is no matter which of them be the hotter. The temperature produced is always the middle temperature between the two, or 125 degrees, in the temperatures already mentioned. Here it is manifest that the same quantity of the matter of heat which makes *two* measures of water warmer by 25 degrees, is sufficient for making *three* measures of quicksilver warmer by the same number of degrees. Quicksilver, therefore, has less *capacity* for the matter of heat than water (if I may be allowed to use this expression) has; it requires a smaller quantity of it to raise its temperature by the same number of degrees.

The inference which Dr. Boerhaave drew from this experiment is very surprising. Observing that heat is not distributed among different bodies in proportion to the quantity of matter in each, he concludes that it is distributed in proportion to the space occupied by each body; a conclusion contradicted by this very experiment. Yet Muschenbroeck has followed him in this opinion.

As soon as I understood this experiment in the manner I have now explained it, I found a remarkable agreement between it and some experiments made by Dr. Martin (Essay on the Heating and Cooling of Bodies) which appeared at first very surprising and unaccountable; but, being compared with this one, may be explained by the same principle. Dr. Martin placed before a good fire, and at an equal distance from it, a quantity of water, and an equal bulk or measure of quicksilver, each of them contained in equal and similar glass vessels, and each having a delicate thermometer immersed into it. He then carefully observed the progress, or celerity, with which each of these fluids was heated by the fire, and raised the thermometers. He found, by repeated experiments, that the quicksilver was warmed by the fire much faster than the water, almost twice as fast; and after each experiment, having heated these two fluids to the same degree, he placed them in a stream of cold air, and found that the quicksilver was always cooled much faster than the water. Before these experiments were made, it was supposed that the quicksilver would require to heat or cool it a longer time than an equal bulk of water, in the proportion of 13 or 14 to one.

But, from the view I have given of Fahrenheit's, or Boerhaave's experiment with quicksilver and water, the above of Dr. Martin's is easily explained. We need only to suppose that the matter of heat, communicated by the fire, was communicated equally to the quicksilver and to the water, but that, as less of it was required for heating the quicksilver, than for heating the water, the quicksilver necessarily was warmed fastest of the two. And when both, being equally heated, was exposed to the cold air to cool, the air at first took their heat from them equally fast, but the quicksilver, by losing the same quantity of the matter of heat that the water lot, was necessarily cooled to a greater degree; it therefore became cold much faster than the water. These experiments of Dr. Martin, therefore, agreeing so well with Fahrenheit's experiment, plainly shew that quicksilver, notwithstanding its great density and weight, requires less heat to heat it, than that which is necessary to heat, by the same number of degrees, an equal measure of equally cold water. The quicksilver, therefore, may be said to have less capacity for the matter of heat. And we are thus taught, that, in cases in which we may have occasion to investigate the capacity of different bodies for heat, we can learn it only by making experiments. Some have accordingly been made, both by myself and others. Dr. Crawford has made a great number of very curious ones, and his Theory of the Heat of Animals is founded partly on some experiments made in this manner, these result of which is given in his book on that subject.

It appears, therefore, from the general result of such experiments, that if we had a thousand masses of matter, of the same size and form, but of different materials, and were to place them all in the same room, until they assumed the same temperature; were we then to introduce into that room a great mass of red hot iron, the heat of which, when communicated with all these different bodies at the same time, might be sufficient for raising the temperature of them all, by 20 degrees; the heat thus communicated from the iron, although it produced an equal effect on each of these bodies, in raising its temperature by 20 degrees, would not however be equally divided or distributed among them. Some of them would attract and retain a much greater quantity of this heat, or matter of heat, than others; and the quantity received by each would not be in proportions totally unconnected with it; and perhaps not any two of them would receive precisely the same quantity, but each, according to its particular capacity, or its particular force of attraction for this matter, would attract and require its own peculiar quantity to raise its temperature by the 20 degrees, or to reduce it to an equilibrium or equality of saturation with the surrounding bodies. We must, therefore, conclude that different bodies, although they be of the same size, or even of the same weight, when they are reduced to the same temperature or degree of heat, whatever that may be, may contain very different quantities of the matter of heat; which different quantities are necessary to bring them to this level, or equilibrium, with one another.

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[Latent Heat]

Fluidity was universally considered as produced by a small addition to the quantity of heat which a body contains, when it is once heated up to its melting point; and the return of such a body to a solid state, as depending on a very small diminution of the quantity of heat, after it is cooled to the same degree; that a solid body, when it is changed into a fluid, receives no greater addition to the heat within it than what is measured by the elevation of temperature indicated after fusion by the thermometer; and that, when the melted body is again made to congeal, by a diminution of its heat, it suffers no greater loss of heat than what is indicated also by the simple application to it of the same instrument.

This was the universal opinion on this subject, so far as I know, when I began to read my lectures in the University of Glasgow, in the year 1757. But I soon found reason to object to it, as inconsistent with many remarkable facts, when attentively considered; and I endeavoured to shew, that these facts are convincing proofs that fluidity is produced by heat in a very different manner.

I shall now describe the manner in which fluidity appeared to me to be produced by heat, and we shall then compare the former and my view of the subject with the phenomena.

The opinion I formed from attentive observation of the facts and phenomena, is as follows. When ice, for example, or any other solid substance, is changing into a fluid by heat, I am of opinion that it receives a much greater quantity of heat than what is perceptible in it immediately after by the thermometer. A great quantity of heat enters into it, on this occasion, without making it apparently warmer, when tried by that instrument. This heat, however, must be thrown into it, in order to give it the form of a fluid; and I affirm, that this great addition of heat is the principal, and most immediate cause of the fluidity induced.

And, on the other hand, when we deprive such a body of its fluidity again, by a diminution of its heat, a very great quantity of heat comes out of it, while it is assuming a solid form, the loss of which heat is not to be perceived by the common manner of using the thermometer. The apparent heat of the body, as measured by that instrument, is not diminished, or not in proportion to the loss of heat which the body actually gives out on this occasion; and it appears from a number of facts, that the state of solidity cannot be induced without the abstraction of this great quantity of heat. And this confirms the opinion, that this quantity of heat, absorbed, and, as it were, concealed in the composition of fluids, is the most necessary and immediate cause of their fluidity.

To perceive the foundation of this opinion, and the inconsistency of the former with many obvious facts, we must consider, in the first place, the appearances observable in the melting of ice, and the freezing of water.

If we attend to the manner in which ice and snow melt, when exposed to the air of a warm room, or when a thaw succeeds to frost, we can easily perceive, that however cold they might be at the first, they are soon heated up to their melting point, or begin soon at their surface to be changed into water. And if the common opinion had been well founded, if the complete change of them into water required only the further addition of a very small quantity of heat, the mass, though of considerable size, ought all to be melted in a very few minutes or seconds more, the heat continuing incessantly to be communicated from the air around. Were this really the case, the consequences of it would be dreadful in many cases; for, even as things are at present, the melting of great quantities of snow and ice occasions violent torrents, and great inundations in the cold countries, or in the rivers that come from them. But, were the ice and snow to melt as suddenly as they must necessarily do, were the former opinion of the action of heat in melting them well founded, the torrents and inundations would be incomparably more irresistible and dreadful. They would tear up and sweep away every thing, and that so suddenly, that mankind should have great difficulty to escape from their ravages. This sudden liquefaction does not actually happen; the masses of ice or snow melt with a very slow progress, and require a long time, especially if they be of a large size, such as are the collections of ice, and wreaths of snow, formed in some places during the winter. These, after they begin to melt, often require many weeks of warm weather, before they are totally dissolved into water. This remarkable slowness with which ice is melted, enables us to preserve it easily during the summer, in the structures called Ice-houses. It begins to melt in these, as soon as it is put into them; but, as the building exposes only a small surface to the air, and has a very thick covering of thatch, and the access of the external air to the inside of it is prevented as much as possible, the heat penetrates the ice-house with a slow progress, and this, added to the slowness with which the ice itself is *disposed* to melt, protracts the total liquefaction of it so long, that some of it remains to the end of summer. In the same manner does snow continue on many mountains during the whole summer, in a melting state, but melting so slowly, that the whole of that season is not a sufficient time for its complete liquefaction.

This remarkable slowness with which ice and snow melt, struck me as quite inconsistent with the common opinion of the modification of heat, in the liquefaction of bodies.

And this very phenomenon is partly the foundation of the opinion I have proposed; for if we examine what happens, we may perceive that a great quantity of heat enters the melting ice, to form the water into which it is changed, and that the length of time necessary for the collection of so much heat from the surrounding bodies, is the reason of the slowness with which the ice is liquefied. If any person entertain doubts of the entrance and absorption of heat in the melting ice, he needs only to touch it; he will instantly feel that it rapidly draws heat from his warm hand. He may also examine the bodies that surround it, or are in contact with it, all of which he will find deprived by it of a great part of their heat; or if he suspend it by a thread, in the air of a warm room, he may perceive with his hand, or by a thermometer, a stream of cold air descending constantly from the ice; for the air in contact is derived of a part of its heat, and thereby condensed and made heavier than the warmer air of the rest of the room; it therefore falls downwards, and its place round the ice is immediately supplied by some of the warmer air; but this, in turn, is soon deprived of some heat, and prepared to descend in like manner; and thus there is a constant flow of warm air from around, to the sides of the ice, and a descent of the same in a cold state, from the lower part of the mass, during which operation the ice must necessarily receive a great quantity of heat.

It is, therefore, evident, that the melting ice receives heat very fast, but the only effect of this heat is to change it into water, which is not in the least sensibly warmer than the ice was before. A thermometer, applied to the drops or small streams of water, immediately as it comes from the melting ice, will point to the same degree as when it is applied to the ice itself, or if there is any difference, it is too small to deserve notice. A great quantity, therefore, of the heat, or of the matter of heat, which enters into the melting ice, produces no other effect but to give it fluidity, without augmenting its sensible heat; it appears to be absorbed and concealed within the water, so as not to be discoverable by the application of a thermometer.

In order to understand this absorption of heat into the melting ice, and concealment of it in the water, more distinctly, I made the following experiments.

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I have, in the same manner, put a lump of ice into an equal quantity of water, heated to the temperature 176, and the result was, that the fluid was no hotter than water just ready to freeze. Nay, if a little sea salt be added to the water, and it be heated only to 166 or 170, we shall produce a fluid sensibly colder than the ice was in the beginning, which has appeared a curious and puzzling thing to those unacquainted with the general fact.

It is, therefore, proved that the phenomena which attended the melting of ice in different circumstances, are inconsistent with the common opinion which was established upon the subject, and that they support the one which I have proposed.

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In the above described common process of freezing water, the extrication and emergence of the latent heat, if I may be allowed to use these terms, is performed by such minute steps, or rather with such a smooth progress, that many may find difficulty in apprehending it; but I shall now mention another example, in which this extrication of the concealed heat becomes manifest and striking.

This example is an experiment, first made by Fahrenheit, but since repeated and confirmed by many others.

He wished to freeze water from which the air had been carefully extracted. This water was contained in small glass globes, about one-third filled, and accurately closed, to prevent the return of the air into them. These globes were exposed to the air in frosty weather, and remained so long exposed, that he had reason to be satisfied that they were cooled down to the degree of the air, which was six or seven degrees below the freezing point. The water, however, still remained fluid, so long as the glasses were left undisturbed, but, on being taken up and shaken a little, a sudden congelation was instantly seen.

It has since been found, by the trials of others, that the experiment will succeed, although the water be not deprived of its air, and that the circumstances the most essentially necessary are, that it be contained in vessels of small size, and preserved carefully from the least disturbance. The vessels, therefore, ought to be covered with paper, or otherwise, to prevent slight motions of the air from affecting the surface of the water. In these circumstances, it may be cooled to six, or seven, or eight degrees below the freezing point, without being frozen; but, if it be then disturbed, there is a sudden congelation, not of the whole, but of a small part only, which is formed into feathers of ice, traversing the water, in every direction, and forming a spongy contexture of ice, which contains the water in its vacuities, so as to give to the whole the appearance of being frozen. But the most remarkable fact is, that while this happens, (and it happens in a moment of time) this mixture of ice and water suddenly becomes warmer, and makes a thermometer, immersed in it, rise to the freezing point.

Nothing can be more inconsistent with the old opinion concerning the cause of congelation than the phenomena of this experiment. It shews that the loss of a little more heat, after the water is cooled down to the freezing point, is not the most necessary and inseparable cause of its congelation, since the water is cooled 6, 7, or 8 degrees below that point without being congealed.

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[Of Vapour and Vaporisation]

A more just explanation will occur to any person, who will take the trouble to consider this subject with patience and attention. In the ordinary manner of heating water, the heating cause is applied to the lower parts of the fluid. If the pressure on the surface be not increased, the water soon acquires the greatest heat which it can bear, without assuming the form of vapour. Subsequent additions of heat, therefore, in the same instant in which they enter the water, must convert into vapour that part which they thus affect. As these additions of heat all enter at the bottom of the fluid, there is a constant production of elastic vapour there, which, on account of its weighing almost nothing, must rise through the surrounding water, and appear to be thrown up to the surface with violence, and from thence it is diffused through the air. The water is thus gradually wasted, as the boiling continues, but its temperature is never increased, at least in that part which remains after long continued and violent boiling. The parts, indeed, in contact with the bottom of the vessel may be supposed to have received a little more heat, but this is instantly communicated to the surrounding water through which the elastic vapour rises.

This has the appearance of being a simple, plain, and complete account of the production of vapour, and of the boiling of fluids; and it is the only account that was given of this subject before I began to deliver these lectures: But I am persuaded that it is by no means a full account of the matter. According to this account, and the notion that was conceived of the formation of vapour, it was taken for granted that, after a body is heated up to its vaporific point, nothing further is necessary but the addition of a little more heat to change it into vapour. It was also supposed, on the other hand, that when the vapour of water is so far cooled as to be ready for condensation, this condensation, or return into the state of water, will happen at once, or in consequence of its losing only a very small quantity of heat.

But I can easily shew, in the same manner as in the case of fluidity, that a very great quantity of heat is necessary to the production of vapour, although the body be already heated to that temperature which it cannot pass, by the smallest possible degree, without being so converted. The undeniable consequence of this should be, an explosion of the whole water, with a violence equal to that of gunpowder. But I can shew, that this great quantity of heat enters into the vapour gradually, while it is forming, without making it perceptibly hotter to the thermometer. The vapour, if examined with a thermometer, is found to be exactly of the same temperature as the boiling water from which it arose. The water must be raised to a certain temperature, because, at that temperature only, is it disposed to absorb heat; and it is not instantly exploded, because, in that instant, there cannot be had a sufficient supply of heat through the whole mass. On the other hand, I can shew that when the vapour of water is condensed into a liquid, the very same great quantity of heat comes out of it into the colder matter by which it is condensed; and the matter of the vapour, or the water into which it is changed, does not become sensibly colder by the loss of this great quantity of heat. It does not become colder in proportion to the quantity of heat obtainable from it during its condensation.

All this will become evident, when we consider with attention the gradual formation of vapour, in consequence of the continued application of a heating cause, and the like gradual condensation of this vapour, when we continue to apply to it a body that is colder.

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I, therefore, set seriously about making experiments, conformable to the suspicion that I entertained concerning the boiling of fluids. My conjecture, when put into form, was to this purpose. I imagined that, during the boiling, heat is absorbed by the water, and enters into the composition of the vapour produced from it, in the same manner as it is absorbed by ice in melting, and enters into the composition of the produced water. And, as the ostensible effect of the heat, in this last case, consists, not in warming the surrounding bodies, but in rendering the ice fluid; so, in the case of boiling, the heat absorbed does not warm surrounding bodies, but converts the water into vapour. In both cases, considered as the cause of warmth, we do not perceive its presence: it is concealed, or latent, and I give it the name of LATENT HEAT.

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[1]Translation: "For the heat is equally distributed throughout, nowhere greater, so that in a cubic foot of gold and of air and of feathers, there is an equal quantity of heat." --CJG

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