drogen peroxide,[1] the electrolytic,[2] or by other methods, we can form the equations

$$(3)\quad \frac{169.89\mathrm{I}}{126.92} + \frac{169.89\ \mathrm{Br}}{79.92} + \frac{169.89\ \mathrm{Cl}}{35.46} = a,$$

$$(4)\quad \frac{234.80\mathrm{I}}{126.92} + \frac{187.80\ \mathrm{Br}}{79.92} + \frac{143.34\ \mathrm{Cl}}{35.46} = b.$$

Solving for Cl and Br in the same manner as above we obtain

$$\text{(VII)}\qquad \mathrm{Cl} = 0.8817a - 0.7976b + 0.2954\,\mathrm{I},$$

$$\text{(VIII)}\qquad \mathrm{Br} = 1.7976b - 1.5166a - 1.2951\,\mathrm{I}.$$

If the chlorine is estimated separately by the acetic acid and manganese or lead peroxide,[3] or other methods, we have equations

$$\text{(IX)}\qquad \mathrm{Br} = 2.3501a - 1.7004b - 0.4386\mathrm{Cl},$$

$$\text{(X)}\qquad \mathrm{I} = 2.7007b - 2.9851a + 3.3857\mathrm{Cl}.$$

And if the bromine[4] is estimated separately, we have the equations

$$\text{(XI)}\qquad \mathrm{Cl} = 0.5358a + 0.3877b - 0.2280\ \mathrm{Br},$$

$$\text{(XII)}\qquad \mathrm{I} = 1.3877b - 1.1706a - 0.7720\ \mathrm{Br}.$$

Equations (I) to (XII) may be written in the following, most concise form:

$$\mathrm{Cl} - \mathrm{Br}\ (\mathrm{I}) \left\{ \begin{array}{l} \mathrm{Cl} = 0.8817a - 0.7976b(+\ 0.2954\ \mathrm{I}) \\ \mathrm{Br} = 1.7976b - 1.5166a(-\ 1.2951\ \mathrm{I}) \end{array} \right.$$

$$\mathrm{Cl} - \mathrm{I}(\mathrm{Br}) \left\{ \begin{array}{l} \mathrm{Cl} = 0.5358a - 0.3877b(-\ 0.2280\ \mathrm{Br}) \\ \mathrm{I}\ \ = 1.3877b - 1.1706a(-\ 0.7720\ \mathrm{Br}) \end{array} \right.$$

$$\mathrm{Br} - \mathrm{I}(\mathrm{Cl}) \left\{ \begin{array}{l} \mathrm{Br} = 2.3501a - 1.7004b(-\ 0.4386\ \mathrm{Cl}) \\ \mathrm{I}\ \ = 2.7007b - 2.9851a(+\ 3.3857\ \mathrm{Cl}) \end{array} \right.$$

SEATTLE, WASHINGTON.

RECENT INVESTIGATIONS IN THERMOCHEMISTRY.[5]

BY THEODORE W. RICHARDS.

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Within a brief space of time, the world has lost two masters of thermochemistry, Marcellin Berthelot and Julius Thomsen. To these great men chemical science owes much; their places in its history are forever secure. Each, by his indefatigable labors, added both new methods and new data to the sum of human knowledge; and upon the broad foundation which they laid, all the subsequent development of thermochemistry must be built. All honor to their memories! It is no discredit to their faithful work that as science progresses many of their methods must be

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[1] Cook, *J. Chem. Soc.*, **1885**, 471.

[2] Specketer, *Z. Elektrochem.*, **4**, 539.

[3] Vortmann.

[4] McCulloch, *Chem. News*, **60**, 259.

[5] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., on Sept. 16, 1909.

subjected to revision and refinement, for mankind approaches precision only little by little, and those workers who come later have the benefit of all that has gone before, with fresh energy and new years with which to improve upon it. In the same way, a few decades hence, others will perhaps remodel the not yet perfect work of the present generation, may possibly marvel at inaccuracies which have escaped our detection, and will have opportunities for the exercise of charity similar to those which fall to our own lot.

It is not necessary to emphasize the importance of thermochemistry, or to trace in detail its history. You know that the first law of energy was applied in this science by Lavoisier and Laplace, and by Hess, before it was generalized by Mayer, Joule and Helmholtz. You are familiar with the fact that Berthelot and Thomsen and Stohmann and others utilized this principle to determine the heats of formation of most common substances with some degree of approximation; and that these data constitute the sum and substance of our knowledge of the heat evolved during chemical reaction.

Before we consider the revision of these multifarious data which is now in progress, it is worth while to pause for a moment and think of their significance.

Thermochemistry is concerned with the total energy-change of a chemical reaction, and not with the change of the free energy, hence it cannot serve as an infallible guide to the tendency of a reaction, for preponderance of free energy, not of total energy, determines the path which a change will take. Nevertheless, in spite of this limitation, thermochemistry includes some of the most important facts of the universe within its scope, both for the theorist and the practical man.

The total heat given out during any chemical change is one of the fundamental thermodynamic data concerning that change. Its exact evaluation is necessary to the complete understanding of the thermodynamics of any reaction, and without an understanding of the thermodynamics of a reaction, the phenomena are only half interpreted. Although free energy change is that which determines the tendency of the reaction, bound energy is also significant, and the interpretation of bound energy is being realized more and more generally as one of the coming problems in thermodynamics. But bound energy is the difference between total energy-change and the free energy-change, so that all these three quantities are as closely connected together as is possible. In short, the accurate determination of thermochemical data is essential to the precise application of thermodynamics to chemistry.

To the practical man, perhaps, the matter takes on a different aspect—although ultimately he, too, will profit more than he can now appreciate from the growth of pure thermodynamics. He is more immediately concerned with the every-day applications of thermochemistry, especially the developments of heat by combustion. Our text-books of chemistry discuss the union of carbon and oxygen with chief emphasis upon the formation of carbon dioxide, but that is the least important practical aspect of the matter. The really essential thing is the liberation of energy, a fact which falls within the province of the thermochemist. Numerous other reactions less striking but no less important, including the maintenance of our own bodily heat, are concerned with the same principles and methods. Hence it is not too much to say that thermochemistry is intimately related with every breath we draw. The accurate evaluation of its fundamental quantities is, therefore, one of the most important fields of scientific advance, because accurate data are needed to provide an adequate basis for precise thinking in an inductive science.

Let us consider systematically the dimensions concerned, in order that we may more clearly appreciate the advances which have been made possible in thermochemical work during the years which have elapsed since Berthelot and Thomsen carried out most of their work. The energy of heat is, of course, calculated as the product of two factors, temperature and heat capacity, and the accuracy of its determination is directly proportional to the accuracy of measurement of each of these dimensions.

The advances in the accurate measurement of temperature during the last thirty years have been very great. In the first place the standard of reference, namely the hydrogen scale, has been fixed with much greater accuracy than at that early time. There is very little evidence as to what the centigrade degree, as used by Thomsen or Berthelot, really meant. In the next place, the vagaries of the glass-mercury thermometer have been studied by Crafts and others with much greater completeness and understanding than in those earlier days. We know now how uncertain its indications may be when it is not properly handled; and we know, also, how to obtain very accurate results from this instrument when it is properly made and carefully used. Again, thermometry has gained through the introduction of new fixed points between the old classic ones of the early history of thermometry; I mean the transition temperatures of bi-component systems. These give a firm basis for a thermometric scale in their neighborhood and thereby contribute to its certainty and definiteness. All these things must be considered in the thermochemistry of to-day and all contribute to an accuracy exceeding that of olden times.

A further gain has to be found in the introduction of the new methods of measuring temperature electrically, which, when properly manipulated, may exceed in accuracy the readings of the mercury thermometer. One must not forget, however, that these methods are subject to their own peculiar and somewhat elusive sources of inaccuracy, and that their use does not yield the unqualified gain which is sometimes attributed to them.[1]

Turning now to heat capacity, we find that to some extent the same considerations apply. Heat capacity is, of course, determined by comparison with a standard substance, and the comparison is made by means of some kind of thermometer. The sources of error are partly eliminated here, however, because the determination is a purely relative one and does not hark back to the absolute standard, as in the case of temperature change. Specific heats are reckoned by finding the rise of temperature in two approximately equivalent masses of substance, one the standard substance and the other the substance to be determined. If the same thermometer is used in each and the quantities of substance are so adjusted that the temperature changes produced by a known quantity of heat energy are nearly the same, the inaccuracies of the thermometer are largely eliminated when the same thermometer is used as a standard in each set of determinations. Errors of reading the thermometer still appear, and indeed the range of inaccuracy here is doubled, because a

[1] Emil Fischer and F. Wrede have made some excellent determinations in this way.

specific heat determination depends upon four thermometer readings whereas temperature change depends upon only two. Obviously, however, an error in the standard interval makes no difference. The degree might really be two degrees and its inaccuracy would cancel. Hence, although the thermometer is used for determining heat capacity, the uncertainties of the determination arise in part from a different source and are chiefly to be traced to the errors of calorimetry, which deserve and will receive detailed consideration in a few minutes.

Before discussing the errors of calorimetry let us for a moment discuss the means of calculating the heat capacity of a given system which have been used in the determinations now accepted by the chemical world. We find upon studying the literature of the subject, that there has been considerable variety of usage, but that the usage has rarely, if ever, been precise. Marignac determined a number of specific heats by means of a kind of calorifer, and Thomsen also determined many by means of his combustion calorimeter, but these were seldom in either case within two-tenths of one per cent. Therefore the values calculated from them could not be expected to be closer than this, if as close, to the truth. Work of others has not yet actually been used. Berthelot relied largely on Marignac's determinations or more commonly adopted very rough approximations by assuming that the heat capacity of the solution is equal to that of a like volume of water—in other words, that the specific heat of a solution is inversely proportional to its specific gravity. This method of calculating may easily yield results several per cent. aside from the truth with concentrated solutions.

Moreover, we find a general haziness concerning the question as to whether the heat capacity of the factors or of the product of reaction is to be used in the calculation. Should one multiply the temperature rise by the heat capacity of the factors in order to obtain the heat evolved, or is it the products which must be considered as having been raised through the range of temperature in question? Only very recently has this question been answered scientifically, and its answer is simply this: either the one or the other may be used, provided that it is used intelligently. When the heat capacity of the factors is used in calculating the result, this result corresponds to the heat evolved by the reaction occurring isothermally at the final temperature attained when the adiabatic change is completed, whatever that may be. On the other hand, when the heat capacity of the products is used, the result corresponds to the heat of isothermal reaction at the initial temperature. When there is no change of heat capacity during the reaction, the results of the two methods will, of course, be identical. In other words, in this last case the heat evolved will be independent of the temperature at which the reaction takes place, according to the well-known thermodynamic rule of Kirchhoff.[1]

Further uncertainty concerning heat capacity arises from the fact that the specific heat of the standard substance, water, changes with the temperature and that therefore no expression for heat capacity is definitely fixed without a qualifying phrase. In order to overcome this disadvantage a proposition of Ostwald's to use the absolute C. G. S. scale has been revived and a convenient standard of heat capacity, namely the capacity

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[1] Richards, THIS JOURNAL, **25**, 209 (1903).

raised one centigrade degree by one joule of energy, has been chosen. This unit fixes the dimension of heat capacity much more definitely than the old uncertain and changing one. Out of respect to the memory of one of the founders of the first law of energy, the name "mayer" has been suggested for this unit and its introduction seems to afford help in teaching as well as to add precision to scientific statement.[1]

In the coming revision of thermochemical data all the early incompletenesses in these respects will be eradicated, and the matter will be put upon the best basis possible to-day.

What now are the chief errors of calorimetry, which affect both the determination of specific heat and of reaction heat?

Any one with any calorimetric experience whatsoever will recognize that the greatest cause of uncertainty in results of this kind is the cooling effect of the surroundings of the calorimeter. The errors of thermometric reading, of the lag of the thermometer behind the temperature of the surrounding medium, and all other uncertainties are trifling compared with this. Therefore precise calorimetry is largely a question of properly correcting for this cause of uncertainty, or else avoiding it altogether. The well-known methods of Rumford and of Regnault as amplified by Pfaundler, serve to a certain extent to correct for the effect of the exchange of heat with the environment. But the former, although it has been much used in thermochemical work, is greatly at fault; and the latter, although far better, is still imperfect. Rumford started his determination as much below the temperature of the air around as he finished above this temperature, supposing that the intake of heat during the first part of the operation would balance the outgo during the latter part. We have been able to show that this is by no means the case—at any rate in a vessel containing a solution and enclosed in a jacket of definite temperature. Hence Rumford's method is not a very close approximation. The Regnault-Pfaundler method depends upon Newton's law of cooling, which under certain circumstances has been shown to be fairly accurate. We must remember, however, that the cooling of the vessel is due to convection and conduction as well as to radiation, so that the exact fulfilment of Newton's law is hardly to be expected. Moreover the evaluation of the rate of cooling depends upon the taking of a number of thermometric readings which are "caught on the wing," as it were, while the thermometer is moving. Hence, although the Regnault-Pfaundler method may serve with sufficient approximation for quick reactions, it still leaves much uncertainty in reactions which extend over many minutes; and even in quick reactions the lag of the cooling correction may introduce some error. Further, many fundamental processes are slow; and among them must be catalogued the determination of specific heat, or heat capacity, because considerable time is needed as a rule to communicate the heat to the substance to be studied.

It was with a view to eliminating these disadvantages that there has recently been put into practice at Harvard a method of calorimetry which wholly eliminates the correction for cooling by causing the temperature of the environment around the calorimeter to change at the same rate as the calorimeter itself. It is surprising that this obvious and easily carried out device had not been applied before. It had, indeed,

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[1] *Proc. Amer. Acad.*, **36**, 327 (1901).

been suggested by S. W. Holman[1] in 1895, although this paper was unknown to me at the time of the first Harvard work. The somewhat similar device used in the respiration calorimeter of Atwater and Benedict, suggested perhaps even before this, is not exactly comparable. In the respiration calorimeter the environment is not essentially changed in temperature. It is merely kept constant, as is also that of the calorimeter, by a suitable quantitative cooling device. Hence, so far as I am aware, the Harvard device was the first one in which the surroundings of the calorimeter were changed in temperature by any considerable amount during the progress of the experiment.

If the surrounding jacket about a calorimeter is thus changed in temperature at exactly the same rate as the temperature of the calorimeter itself, it is obvious that the calorimeter will neither gain nor lose heat from its equally hot surroundings, excepting for the negligible quantity of heat required to warm the small quantity of air immediately in contact with it inside the jacket. Thus a calorimetric reaction may be made really adiabatic.

Obviously there are several ways in which the outside water jacket in a calorimeter might be heated in order to accomplish this purpose. The simple device of pouring in hot water might be employed, or the water might be warmed by an electrically heated resistance coil, or the jacket itself might be made the scene of a chemical reaction of the same speed and thermal intensity as that within the calorimeter itself.

Of these and other methods which suggested themselves the last named seemed the most convenient and suitable for a chemical laboratory. It has the special advantages that before the beginning of operations all the apparatus and material employed may be at the temperature of the room; that the maximum temperature attained may be easily calculated with great nicety; that no point in the system can ever exceed this maximum temperature, if the reaction is suitably chosen; and that the speed of the reaction may be simply regulated by a stop cock admitting one of the reacting substances. A reaction easily regulated and well suited to this purpose, namely, the neutralization of an alkali with an acid, was chosen for this purpose.

The form of apparatus originally devised consisted of a lower jacket containing alkali and a separate movable lid. More recently we have found it convenient to enclose the calorimeter wholly in a water-tight vessel—a sort of submarine, provided with suitable conning towers or periscopes.[2] This water-tight compartment is wholly immersed in the alkali to which is added, little by little, sulphuric acid in order to keep the bath precisely at the same temperature as the interior, however much this may be changed. Violent agitation of the warming alkali is necessary in order that the heat may be quickly distributed throughout the whole mass, and the interior of the calorimeter must be agitated also more energetically than has usually been the custom, if great precision is needed. In passing, I may state that we have evidence showing that in the past no one has stirred his calorimeter violently enough. The burettes delivering the sulphuric acid into the alkaline environment

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[1] *Proc. Am. Acad.*, **31**, 252 (1895).

[2] A device of this kind was employed by Richards and Forbes, *Publications of the Carnegie Inst.*, **56**, 52 (1906).

are graduated in tenths of degrees, instead of in cubic centimeters, so that a small deficiency in temperature may be instantly corrected with a minimum of mental arithmetic.

This form of chemical calorimeter serves not only to determine with great accuracy specific heats, but also to estimate the thermal output of all forms of chemical reactions. With it series of determinations of many kinds are in progress.

In the first place let me describe somewhat more closely the determination of specific heat with this apparatus, because upon this determination the calculation of all other thermochemical results must depend. Within the platinum calorimeter, enclosed in its submarine, is immersed a small platinum bottle; and inside of this bottle a carefully measured chemical reaction is allowed to take place which communicates its heat to the calorimeter. By placing in the calorimeter, in the first place water, and in the next place the unknown liquid whose specific heat is to be determined, and each time allowing the measured reaction to occur within the innermost platinum bottle, a direct comparison of the specific heats of the standard and the unknown liquid is obtained. As the results agree within one-twentieth of one per cent., the average of many experiments must be much nearer than this, and it is not unreasonable to believe that the results thus obtained are at least five times as accurate as those of Thomson or Marignac.

Having used this device and method for determining the specific heats of liquids, it is now possible to proceed with the more accurate evaluation of reactions in which liquids take part. In two recent investigations the heats of neutralization of the acids and alkalis on the one hand and the heats of solution of metals in acids on the other hand have been studied. Time does not permit the detailed statement of the various precautions necessary in these determinations. The former problem is of special interest because of its relation to the theory of electrolytic dissociation, and our revision of this work was prompted by the desire to discover the extent of the deviation of the several results for strong acids from the constant value, 137 calories or 57 kilojoules. Several unexpected points were brought out in the investigation, the most important being the irregularities in the results produced by the unequal distribution in heat during mixing and also the grave errors caused in previous results by the presence of carbonate in the alkali. The investigation is not yet finished, but has already shown that many of the accepted results are much in error even for this simple process of neutralizing an acid by an alkali.

The heats of solution of metals in acids are among the most essential and fundamental of thermochemical data. The heats of formation of all the metallic compounds depend upon them, because through them the heat values are referred back to the element. Hence it is highly important for exactness in thermochemistry that these values be determined with great precision.

As a matter of fact, in the past certain difficulties have interfered with the perfection of the measurements. First and foremost among these is the fact that the heat of solution of a metal requires much time, and therefore the always somewhat uncertain correction for cooling in the usual method becomes a serious fraction of the whole rise of temperature. In the second place, the method generally used—namely, the plunging of a weighed sheet of metal into acid, and then withdrawing it, checking the reaction as soon as possible, and determining the amount dissolved by loss in weight—is open to serious criticism. It is impossible that the withdrawal should be so quick as to introduce no error in the result.

The new method of adiabatic calorimetry, recently used at Harvard, seems to be especially suitable for such cases as this. With it cadmium, zinc, magnesium, aluminium and iron have already been investigated, and very concordant and satisfactory results have been obtained. Here again much greater purity of material than has been usual in work of this sort was sought, and the results justify the trouble thus taken. There can be no doubt that in these cases also the older work was defective.

The heats of combustion of organic substances form another very important field for thermochemical research. These reactions carried out in the calorimetric bomb of Berthelot seemed especially suitable for the application of the new method of calorimetry, and formed indeed one of the first series of experiments to which it was applied. The combustion of solid substances such as sugar presents no difficulty and imagination can easily picture the way in which this process might be carried out in an adiabatic calorimeter. Several long series of experiments with typical substances of this sort have been made in order to test the method, with satisfactory results.[1] The combustion of liquids is a more difficult problem. As you well know, Thomsen endeavored to burn liquids by first vaporizing them with the help of electrically generated heat in his so-called "universal burner." We now know that some of the superfluous heat from the electric coil must have found its way into the calorimeter, so that these results are usually too high. Berthelot and Stohmann, on the other hand, determined the heat of combustion of organic liquids by saturating cellulose with the liquid, which was then ignited in the bomb. This latter method of procedure is evidently open to the error caused by a varying loss of the organic liquid by evaporation. Not all the vapor of the organic liquid spread throughout the bomb is capable of being burnt, hence Berthelot's results for volatile liquids are probably all too low. The truth would be expected to lie somewhere between them, Thomsen's results for the more volatile liquids being probably the more accurate because there the accidental heating from his apparatus was unimportant, and Berthelot's results for the less volatile liquids being better because there the loss through evaporation would cause less error.

We sought to overcome these difficulties by enclosing the organic liquid in a small, very thin glass bulb, flattened on the sides and completely full of liquid. No difficulty is found in making such bulbs, and they will stand several hundred atmospheres of pressure without bursting, if completely full of liquid, because the glass of the flattened sides is sufficiently flexible to permit of considerable compression. These closed glass bulbs were put inside the bomb in a very small platinum crucible, and upon a thin glass shelf above them was placed a small weighed quantity of powdered sugar. The sugar was ignited first in the usual way. This exploded the bulb and instantly lighted the vapor of the liquid at all points so that none escaped combustion. In this way we have been able to show that the heat of combustion of volatile organic liquids is as a rule distinctly higher than Stohmann and Berthelot supposed it to be.

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[1] *Proc. Amer. Acad.*, **42**, 573 (1907).

We have unquestionable evidence that complete combustion of their vapor has at last been attained. These methods open the way to an unlimited amount of further experimentation, and promise to afford results upon which interesting theoretical considerations may be founded.

It is a pleasure to acknowledge my thanks to my several assistants, Professor A. B. Lamb, and Drs. L. J. Henderson, G. S. Forbes, H. L. Frevert, A. W. Rowe, R. H. Jesse, Jr., and L. L. Burgess for their expert assistance in these protracted and often tiresome researches, as well as to express my obligations to the Cyrus M. Warren Fund of Harvard University, the Rumford Fund of the American Academy of Arts and Science and especially to the Carnegie Institution of Washington, for generous pecuniary help in the prosecution of the work.

Before closing let me review briefly the recent advances in thermochemistry which I have attempted to enumerate. In the first place, the thermometric scale has been far more definitely fixed than it was thirty years ago. In the next place, the determination of specific heat and therefore of heat capacity has been put upon a scientific basis and its precise treatment in the calculation of thermochemical results has been pointed out. In the next place the most serious correction for all thermochemical results in the past, namely the cooling correction, has been entirely obviated by the use of the method preventing loss of any heat from the calorimeter by enclosing the latter in a jacket of similarly changing temperature. Again the necessity for more active agitation of the contents of the calorimeter has been demonstrated, and the necessity of the use of very pure materials has been put beyond question. In every case the effort has been made to insure the completeness of the reaction and to correct for any side reactions which may take place at the same time, so that the final results may represent truly the data sought. In short the effort has been made to apply to these fundamental figures concerning chemical energetics the same kind of precision which has recently been attempted in the revision of atomic weights; and although on account of the greater complexity of the problem the percentage accuracy thus far reached has probably not equaled that in the case of atomic weights, one cannot help thinking that the proportional gain over the previous investigations is perhaps as great in this case as in the other.

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NOTE.

The Nomenclature of H_2S.—Although it takes a great deal of time to substitute a new name for an old one in a science, it seems as if efforts should be made from time to time to introduce uniformity or simplicity where possible. The names hydrogen sulphide and sulphuretted hydrogen, besides being cumbersome, give no suggestion of the acidic nature of H_2S and it seems as if they should be dropped. Following German, French or Spanish usage it might be designated *sulphydric* acid, but the English usage would be *hydrosulphuric* acid, comparable to other binary acids like hydrochloric, etc. I do not see any good reason, however, why this could not be shortened simply to *hydrosulphic*, or in the