These results show conclusively that the separation of mercury from arsenic, antimony, and copper, by the use of tartaric acid and potassium cyanide is more complete and consequently more accurate than by the use of ammonium sulphide.

Chism's method also was tried on the tetrahedrite, with good results. This seems to prove this method very good for ores running low in mercury.

The results obtained by Chism's method were 0.27 per cent. and 0.33 per cent. of mercury.

As this work was carried out under the suggestion and guidance of Professor E. H. Miller, it is but just and proper, that any merit which it may possess be associated with his name.

QUANTITATIVE LABORATORY,
May, 1902.

NOTE CONCERNING THE CALCULATION OF THERMOCHEMICAL RESULTS.

By Theodore William Richards.

Received December 10, 1902.

It is well known that the heat capacities of the majority of reacting substances change during their reaction. The magnitude of these changes and their significance are nevertheless often neglected.

A serious error may arise from this neglect. For example, according to the results of Thomsen, the neutralization of an approximately half normal solution of sodium hydroxide by an equivalent solution of hydrochloric acid involves an increase of heat capacity of 1.27 per cent.[1] The question now arises, since the solutions themselves are the capacities being warmed, What value for the total heat capacity shall be used in the calculation of the heat of reaction? Obviously the energy-change will be found to be 1.27 per cent. greater if the final, rather than the initial, heat capacity is used. The answer to this question is variously given in the different authorities upon thermochemistry. Ostwald and Luther in their admirable handbook[2] use the sum of the initial heat capacities; Thomsen often uses the capacity of the water alone; Berthelot commonly considers the capacity as equal to that

---

[1] Thomsen : "Thermochemische Untersuchungen," I, p. 67 (1882).

[2] Ostwald-Luther : *Physiko-Chemische Messungen*, (1902), p. 214.

of the same volume of water, and Wiedemann and Ebert,[1] as well as Traube,[2] recommend similar crude approximations.

It is probable that all of these writers understood wholly the conditions involved by their respective methods, but it is certain that they have not made this understanding clear to the public. The resulting frequently observed confusion among students of physical chemistry concerning this point has therefore led to the present paper. This paper does not pretend to claim originality; it is designed rather to further a general comprehension of the subject, and thus to add to precision of work and statement.

Obviously, since changing heat capacity means changing heat of reaction with changing temperature,[3] the precise thermochemical reaction should be conducted isothermally. In many cases, Waterman's method, which consists in dropping into a warming mixture known weights of cold material and vice versa,[4] may make this isothermal performance possible. Here the calculation is very simple, for the heat capacity to be considered is merely that of the compensating foreign material,—unless indeed this substance in the act of mixing changes its own heat capacity. Waterman's method is, however, rarely employed; the more usual method is to allow the reacting substances to raise or lower the temperature of their resulting mixture adiabatically, that is, without releasing or gaining heat. Nothing could be simpler than the calculation of this adiabatic process in terms of an isothermal one; and this calculation at once clears away the confusion before mentioned.

Imagine for the sake of definiteness a warming reaction. According to the first law of energy, the isothermal evolution of heat in the reaction may be as well measured in two stages as in one. Hence, after the reaction is completed without loss of heat, the mixture may be cooled down to the original temperature; and the heat given out during this cooling will be the total heat of reaction at that temperature. This value will be found by multiplying the heat capacity of the *product* of the reaction by the change of temperature, since it is this product which is to be cooled.

The proceeding may be represented graphically by the right-

---

[1] Wiedemann-Ebert: *Physikalisches Praktikum* (1899).

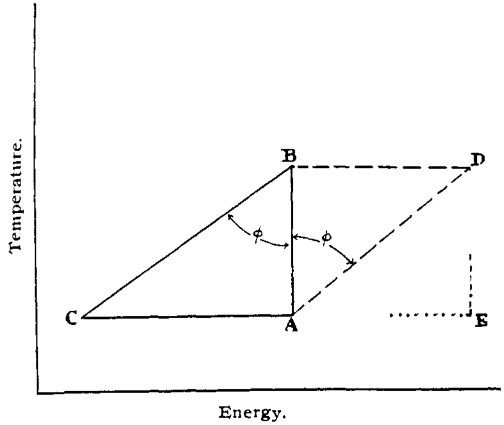
[2] Traube's (trans. Hardin): "Physical Chemical Methods," 1898.

[3] Kirchhoff's Law; see also Thomsen: "Thermochemische Untersuchungen," I, p. 65 (1882).

[4] Waterman: *Phys. Rev.*, **4**, 161 (1896); see also Cady: *Jour Phys. Chem.*, **2**, 561 (1898).

angled triangle A B C in the accompanying diagram, in which A represents the initial state of the system, A B the adiabatic process, B C the cooling process, and A C the desired isothermal loss of energy.

Does this demonstration, proving that the capacity of the *products* must be used in order to obtain the true heat of reaction at the initial temperature, render valueless a knowledge of the capacity of the factors? Not at all; for it is easy to show that the heat of reaction computed from the specific heats of the *factors* is that corresponding to the *final* temperature. Let us consider the same reaction as before, between the same temperatures. The adiabatic effect will be precisely the same as before. But in order that the heat capacities of the factors may be used, and the total process still be isothermal, it is obvious that the factors must first be cooled from a temperature which is to be the final one, to that from which the adiabatic reaction is to start. This cooling, represented above by the line D A, is immediately followed by the adiabatic reaction A B, which brings the system to the same temperature as D. During this double process, the system at the final temperature has lost an amount of energy represented by D B, all of which was removed by the cooling of the factors.



In brief, *the total heat capacity of the product must be multiplied by the change in temperature in order to compute the heat of reaction at the initial temperature, while the total heat capacity of the factors must be so multiplied in order to compute the heat of reaction at the final temperature.* This statement applies to a cooling reaction as well as to a warming reaction. If, as is often the case, the total energy change at an average temperature is desired, the average of the two total heat capacities must be used in the computation. If the two factors have at first different temperatures, their effects must be computed separately and the resulting heat of reaction must be referred to the final temperature. When there is an accidental outside warming or cooling effect, the corrected temperatures should be used.

A slight inexactness lies in the italicized statement, due to the fact that specific heat itself is variable with temperature. Therefore, the heat capacities of the initial and final systems are not in reality perfectly constant, and the lines B C and D A should not be perfectly straight. This deviation is nevertheless usually very slight in dilute aqueous solutions; and until the whole body of physicochemical data attains a much greater degree of accuracy than at present, it may be neglected.

Evidently the quadrilateral figure C A B D may be used to demonstrate trigonometrically the rule of Kirchhoff—the familiar relation which lies at the basis of the question treated in this paper. The reaction may proceed from A to B by two simple indirect paths. According to one, the reaction may be allowed to take place isothermally, at the lower temperature, involving the loss of energy, A C, and the products may then be warmed to a higher temperature involving a gain of energy, C B, while according to the other the factors may be warmed to the higher temperature, A D, and the reaction there allowed to proceed isothermally to B by the loss of energy, D B. In this demonstration it is of course unnecessary to place B exactly over A, a condition which ensues only when the higher temperature is that actually attained by the adiabatic reaction. Obviously, from inspection of the diagram,

$$\mathrm{CE} = \mathrm{CA} + \mathrm{AB} \tan \phi' = \mathrm{BD} + \mathrm{AB} \tan \phi\,;$$
$$\mathrm{CA} - \mathrm{BD} = \mathrm{AB}\,(\tan \phi - \tan \phi').$$

Now $(\mathrm{CA} - \mathrm{BD}) = U_T - U_{T-t}$, the difference between the heats of reaction at the two temperatures; $\tan \phi$ or $\frac{\mathrm{CA}}{\mathrm{AB}}$ represents the heat capacity of the products (K_2); $\tan \phi$ or $\frac{\mathrm{BD}}{\mathrm{AB}}$ represents the heat capacity of the factors (K_1); and the vertical distance AB represents the change of temperature. Hence this trigonometrical statement at once reduces to the well-known equation

$$K_2 - K_1 = \frac{U_T - U_{T+t}}{t}.$$

An important object of the discussion is to emphasize the necessity of reducing all thermochemical data to their isothermal values at some definite convenient temperature (preferably 20°), in order that they may be strictly comparable.

As an evidence of frequent laxity in this respect, the often quoted figures for the heat of neutralization of hydrochloric, hydrobromic and hydriodic acids may be cited. Thomsen records as the three values to be compared 13,740, 13,748, 13,676 calories[1] (or better, 57.46, 57.49 and 57.19 kilojoules), if the base is sodium hydroxide. On seeking the original data, it is easily found that the first corresponds to a rise of temperature from about 18° to 22°, the second to a rise from 16.6° to 18.6°, and the third to a rise from 17.5° to 19.5°. In the calculation, the approximate heat capacities of the factors were used in each of the three cases. If all these results are reduced to the isothermal value at 20°, the heats of neutralization become respectively 13,820, 13,690, and 13,650 calories (or 57.8, 57.2, and 57.1 kilojoules). The order of magnitude in the cases of hydrochloric and hydrobromic acids is reversed by the new calculation, and they have been separated by a whole per cent.[2] Even these values cannot be called ultimate, for the heat capacities of most of the solutions concerned are not accurately known, the value of Thomsen's centigrade degree in terms of the International Standard is not recorded, nor do we know how nearly the 20° points on the thermometers correspond with the true point.

It is hoped that these critical remarks will not be considered as depreciating the admirable and important work of Thomsen, Berthelot, and others. For many purposes the approximate values suffice, and if the greatest precision had been aimed at, the bulk of the results must have been much smaller, an outcome which would have been a real misfortune. In some cases the correction for cooling may have caused even a greater uncertainty than those considered above, and great care about heat capacity would have been labor thrown away. It is not at all surprising that this admirable work should not have attained a degree of

---

[1] "Thermochemische Untersuchungen," I, pp. 104, 155, 63, 67 (1882).

[2] The apparent inconsistency of the results on page 63 of Thomsen's work is easily explained by noting that there the heat capacity of the *product* was used in the calculation. The hydrochloric acid was in every case twice the strength of the other acids, hence the heats of dilution (which are, however, very small) should be included for an exact comparison.

accuracy sufficient for the more exacting needs of the present day.

In this connection it is appropriate to call attention to the fact that not all of the values for heat of reaction commonly given in the tables correspond to consistent atomic weights, although most of them are calculated upon the basis of $O = 16.000$. A praiseworthy service would be rendered by any careful computer who would take the trouble to recalculate all the data and express the results for 20° C. in terms of the most accurate table of atomic weights and the admirable c. g. s. unit of energy, the kilojoule, adopted by Ostwald.[1] The latter's preliminary tables, although an important step in the right direction, are much hampered in their usefulness by their limited scope and the frequent omission of significant decimals.

SUMMARY.

This paper is a plea for greater accuracy in the calculation of thermochemical data. The importance of a uniform temperature for comparison and consistent atomic weights are especially emphasized. It is shown that when the heat capacity of the factors is used in the calculation, the resulting heat of reaction corresponds to the final temperature attained, while if the heat capacity of the products is used in the calculation, the result corresponds to the initial temperature.

NOTES.

Note on the Occurrence of Alum as an Efflorescence on Bricks.—Some time ago I was consulted as to the cause of the discoloration of certain white bricks used in the construction of a large office building in this city. It was readily ascertained to be due to the formation and subsequent oxidation of ferrous sulphate. To remove the stain, some of the bricks were treated with sulphuric acid and then thoroughly washed with water. After they had been dried, a white efflorescence appeared on their surface, and it was found to consist for the most part of potash alum. As I have not been able to find any reference to the occurrence of this salt among the sulphates which are known to exist in similar efflorescences, it occurred to me that a quantitative analysis of the product might be of interest.

Owing to the lack of material the analysis made was incom-

---

[1] Ostwald's "Grundriss der Allgemeinen Chemie," p. 253 (1899).