generate a current of electricity through the solution and the metallic part of the circuit. The reaction as before is com­pletely expressed by the chemical equation Zn+H2SO4 = ZnSO4H+2, the initial and final systems being exactly the same as in the first case; yet the amount of heat generated by the action is much smaller, a quantity of the intrinsic energy having been converted into electrical energy. This electrical energy, however, is equivalent to the heat which has disappeared, for it has been shown experimentally that if it is converted into heat and added to the heat actually evolved, the total quantity of heat obtained is exactly equal to that produced by the direct dissolution of the zinc in the absence of platinum.

§3. The following conditions have to be considered as affecting in a greater or less degree the intrinsic energy of the initial and final systems:—

(1) Dilution of solutions.

(2) Physical state.

(3) Change of volume.

(4) Allotropic modifications.

(5) Temperature.

(1) Generally speaking, there is a considerable thermal effect when a substance is dissolved in water, and this effect varies in magnitude according to the amount of water employed. It is only, however, when we deal with comparatively concentrated solutions that the heat-effect of diluting the solutions is at all great, the heat-change on diluting an already dilute solution being for most practical purposes negligible. In dealing, therefore, with dilute solutions, it is only necessary to state that the solutions are dilute, the exact degree of dilution being unimportant. It occasionally happens that a change in dilution affects the chemical action that occurs. Thus if concentrated instead of dilute sulphuric acid acts upon zinc, the action takes place to a great extent not according to the equation given above, but according to the equation

Zn +2H2SO4 = ZnSO4+SOa+2H2O,

sulphur dioxide and water being produced instead of hydrogen. Here we have a different final system with a different amount of intrinsic energy, so that the thermal effect of the action is alto­gether different.

(2) The physical state of the reacting substances must be con­sidered, since comparatively large amounts of heat are absorbed on fusion and on vaporization. Thus the heat of fusion of ice (for H2O=18 g) is 1440 cal., and the heat of vaporization of water at 100°, for the same quantity, 9670 cal.

(3) The effect of change of volume against external pressure (due to production or consumption of mechanical energy) may be neglected in the case of solids, liquids or solutions, but must usually be taken into account when gases arc dealt with. Each gramme­molecule of a gas which appears under constant pressure during a chemical action *(e.g.* hydrogen during the action of zinc on dilute sulphuric acid) performs work equivalent to 580 cal. at the ordinary temperature, which must be allowed for in the thermochemical calculation. A similar correction, *of* opposite sign, must be made when a gramme-molecule of gas disappears during the chemical action.

(4) When a substance—*e.g.* carbon, phosphorus, sulphur—exists in allotropic forms, the particular variety employed should always be stated, as the conversion of one modification into another is frequently attended by a considerable thermal effect. Thus the conversion of yellow into red phosphorus evolves about one-sixth of the heat of combustion of the latter in oxygen, and so the know­ledge of which variety of phosphorus has been employed is of essential importance in the thermochemistry of that element.

(5) The influence of temperature on the thermal effect of a chemical action is sometimes considerable, but since the initial and final temperatures, which alone determine the variation in the thermal effect, are in almost all cases within the ordinary laboratory range of a few degrees, this influence may in general be neglected without serious error.

§ 4. *Methods.—*In order to estimate the thermal effect of any chemical process, use is made of the ordinary methods of calori­metry, the particular method being selected according to the nature of the chemical action involved. In almost every case the method of mixture (see Calorimetry) is employed, the method of fusion with Bunsen’s ice-calorimeter being only used in special and rarely occurring circumstances.

As a very great number of important chemical actions take place on mixing solutions, the method for such cases has been thoroughly studied. When the solutions employed are dilute, no water is placed in the calorimeter, the temperature-change of the solutions themselves being used to estimate the thermal effect brought about by mixing them. Known quantities of the solutions are taken, and the temperature of each is ac­curately measured before mixing, the solutions having been allowed as far as possible to adjust themselves to the same temperature. The change of temperature of the solutions after the mixing has taken place is then observed with the usual precautions. It is of course in such a case necessary to know the specific heat of the liquid in the calorimeter. Thomsen by direct experiment found that the heat-capacity of a dilute aqueous solution diverged in general less than 1 per cent. from the heat-capacity of the water contained in it, the divergence being sometimes in one sense, sometimes in the other. He there­fore abstained from determining for each case the specific heats of the solutions he employed, and contented himself with the above approximation. Berthelot, on the other hand, assumed that the heat-capacity of an aqueous solution is equal to that of an equal volume of water, and calculated his results on this assumption, which involves much the same uncertainty as that of Thomsen. Since thermochemical measurements of this type may be frequently performed with an error due to other causes of much less than 1 per cent., the error introduced by either of these assumptions is the chief cause of uncertainty in the method.

The calorimeter used for solutions is usually cylindrical, and made of glass or a metal which is not attacked by the reacting substances. The total quantity of liquid employed need not in general exceed half a litre if a sufficiently delicate thermometer is available. The same type of calorimeter is used in determining the heat of solution of a solid or liquid in water.

Combustion calorimeters are employed for observing the heat generated by the brisk interaction of substances, one of which at least is gaseous. They are of two kinds. In the older type the combustion chamber (of metal or glass) is sunk in the calori­meter proper, tubes being provided for the entrance and exit of the gaseous substances involved in the action. These tubes are generally in the form of worms immersed in the water of the calorimeter. In the newer type (which was first proposed by Andrews for the combustion of gases) the chemical action takes place in a completely closed combustion chamber of sufficient strength to resist the pressure generated by the sudden action, which is often of explosive violence. The steel com­bustion chamber is of about 250 c.c. capacity, and is wholly immersed in the calorimeter. To withstand the chemical action of the gases, the “ calorimetric bomb ” is lined either with platinum, as in Berthelot’s apparatus, or with porcelain, as in Mahler’s. For ordinary combustions compressed oxygen is used, so that the combustible substance bums almost in­stantaneously, the action being induced by means of some electrical device which can be controlled from without the calori­meter. The accuracy of heats of combustion determined in the closed calorimeter is in favourable cases about one-half per cent. of the quantity estimated.

§ 5. *Units and Notation.—*The heat-units employed in thermo­chemistry have varied from time to time. The following are those which have been in most general use :—

Small calorie or gramme calorie .... cal.

Large or kilogramme calorie Cal.

Centuple or “ rational ” calorie . . . . K.

The centuple calorie is the amount of heat required to raise 1 g. of water from 0o C. to 100° C., and is approximately equal to 100 cal. The large calorie is equal to 1000 cal. In view of the not very great accuracy of thermochemical measurements, the precise definition of the heat-unit employed is not a matter of special importance. It has been proposed to adopt the *joule,* with the symbol j, as thermochemical unit for small quantities of heat, large amounts being expressed in terms of the *kilojoule,* Kj=1000 j. (For the exact relation between these heat-units, see Calorimetry.) For ordinary thermochemical work we may adopt the relation 1 cal. = 4· 18 j, or 1 Cal. = 4· 18 Kj.

Except for technological purposes, thermochemical data are not referred to unit quantity of matter, but to chemical quantities *—i.e.* to the gramme-equivalents or gramme-molecules of the