arc practically contemporaneous with the recognition of that law, and without it the science could scarcely have reached the degree of development which it rapidly attained. Thomas Andrews and, especially, G. H. Hess (1840) were the first who systematically investigated thermochemical effects in solution, and arrived at conclusions from their experimental data which still possess validity. Andrews, for example, found that when a series of acids were under similar conditions used to neutralize a given amount of a base, the quantity of heat evolved on the neutralization was the same in all cases. Hess, from his work, arrived at the converse conclusion, that when a series of bases were used to neutralize a given amount of an acid, the heat of neutralization was always the same. Both of these statements are correct when the powerful mineral acid and bases are con­sidered, exceptions only arising when weak acids and bases are employed. Again, Andrews discovered that when one metal displaces another from solution of its salts (e.g. zinc with solu­tions of copper salts), the thermal effect is practically independent of the nature of the acid radical in the salt employed. Andrews likewise found that when the heat evolved on the displacement from its salts of a metal M' by a metal M is added to the heat of displacement of another metal M" by M', the sum is equal to the heat which is evolved on the direct displacement of M" from its salts by Μ. This affords an example of a principle which had been stated by Hess in a very general form under the name of the *Law of Constant Heat Sums—*namely, that the thermal effect of a given chemical action is the same, inde­pendently of the character and number of the stages in which it takes place. Thus, in the above example, it is immaterial whether M displaces M" from its salt directly, or whether M first displaces M', which is then used to displace M'. This important principle is a direct consequence of the law of the conservation of energy, but was discovered independently by Hess from accurate experiment.

Hess employed this principle to determine indirectly the *heat of formation* of compounds from their elements, when this magni­tude, as is generally the case, was inaccessible to direct measure­ment. Thus the heat of formation of anhydrous zinc sulphate, ZnSO4, which cannot be determined directly, may be arrived at by summation (in Hess’s units) as follows:—

Oxidation of Zn to ZnO 5291 units

S to.SOs 6384 „

Dissolution of SOs in much water 2566 „

„ ZnO in the resulting aqueous H2SO<. . 1609 ,,

J 5850 .>

Deduct heat of dissolution of anhydrous ZnSO< . . 1193 „

Heat of formation of ZnSO4 from Zn, S, and 4O= · 14657 „

Heats of formation are still determined for the most part in a precisely similar manner.

Hess also stated another principle on empirical grounds, which, although admitting of many exceptions, is of consider­able utility and significance. It had been known long before his time that when solutions of neutral salts were mixed, and no precipitate resulted, the mixed solution was also neutral. Hess now observed that in the process of mixing such neutral solutions no thermal effect was produced—that is, neutral salts in aqueous solution could apparently interchange their radicals without evolution or absorption of heat. These experimental results were generalized by him under the title of the *Law of Thermoneutrality.*

After the investigations of Hess and Andrews, a great deal of excellent experimental work was performed by P. A. Favre and J. T. Silbermann, whose chief theoretical achievement was the recognition that the heat of neutralization of acids and bases was additively composed of two constants, one deter­mined by the acid and the other by the base. This deduction harmonized the observations of Andrews and of Hess previously alluded to, and also accounted satisfactorily for the Law of Thermoneutrality.

Julius Thomsen was the first investigator who deliberately adopted the principle of the conservation of energy as the basis of a thermochemical system. His thermochemical work was begun in 1853, but most of his experiments were performed in the years 1869-82, the whole being published collectively, under the title *Thermochemische Untersuchungen,* in four volumes. Somewhat later than Thomsen, Marcellin P. E. Berthelot began (in 1873) a long series of thermochemical determinations. It is to these two investigators and their pupils that most of our exact thermochemical data are due.

Thomsen and Berthelot independently enunciated a generaliza­tion (commonly known as Berthelot’s *Third Principle,* or *Principle of Maximum Work),* which may be stated in brief as follows:—Every pure chemical reaction is accompanied by *evolution* of heat. Whilst this principle is undoubtedly applic­able to the great majority of chemical actions under ordinary conditions, it is subject to numerous exceptions, and cannot therefore be taken (as its authors originally intended) as a secure basis for theoretical reasoning on the connexion between thermal effect and chemical affinity. The existence of reactions which are reversible on slight alteration of conditions at once invalidates the principle, for if the action proceeding in one direction evolves heat, it must absorb heat when proceeding in the reverse direction. As the principle was abandoned even by its authors, it is now only of historical importance, although for many years it exerted considerable influence on thermo­chemical research.

§2. From the standpoint of the law of conservation of energy, the relation between chemical and thermochemical action bears the following aspect :—A given amount of any sub­stance under given conditions possesses a perfectly definite amount of intrinsic energy, and, no matter what chemical and physical transformations the substance may undergo, it will, when it returns to its original state, possess the original amount of intrinsic energy. If we consider now the transformation of one system of chemical substances into another system under specified conditions, we shall find that in general the intrinsic energy of the second system is different from the intrinsic energy of the first. Let us assume, as is commonly the case, that the intrinsic energy of the initial system is greater than that of the final system. When the first system then is transformed into the second, the excess of energy which the former possesses must appear in the shape of heat, light, electrical energy, mechanical energy, &c. It is for the most part a simple matter to obtain the excess of energy entirely in the form of heat, the amount of which is easily susceptible of measurement, and thus the existence of thermochemistry as a practical science is rendered possible. Since the intrinsic energies of the two systems under given conditions are invariable, the difference between them is constant, so that the heat evolved when the first system is converted into the second is equal to that ab­sorbed when the second system is re-transformed into the first (cf. Lavoisier and Laplace, *ante,* § 1). The total thermal effect, too, which is associated with the transformation, must be the same, whether the transformation is conducted directly or in­directly (Hess’s *Law of Constant Heat Sums),* since the thermal effect depends only on the intrinsic energies of the initial and final systems.

Since the intrinsic energy of a substance varies with the conditions under which the substance exists, it is necessary, before proceeding to the practical application of any of the laws mentioned above, accurately to specify the conditions of the initial and final systems, or at least to secure that they shall not vary in the operations considered. It is also a necessary condition for the application of the preceding laws that no form of energy except heat and the intrinsic energy of the substances should be ultimately involved. For example, when metallic zinc is dissolved in dilute sulphuric acid with production of zinc sulphate (in solution) and hydrogen gas, a definite quantity of heat is produced for a given amount of zinc dissolved, pro­vided that the excess of energy in the initial system appears entirely as heat. This provision may not always be fulfilled, since by placing the zinc in electrical contact with a piece of platinum, likewise immersed in the sulphuric acid, we can