those hydrocarbons with positive heat of formation generate less heat on burning than the elements from which they were formed, whilst those with a negative heat of formation generate more. Thus the heat generated by the combustion of acetylene, C2II2, is 316000 cal., whereas the heat of combustion of the carbon and hydrogen composing it is only 256900 cal., the difference being equal to the negative heat of formation of the acetylene.

For substances consisting of carbon, hydrogen and oxygen, a rule was early devised for the purpose of roughly calculating their heat of combustion (J. J. Welter's rule). · The oxygen contained in the, compound was deducted, together with tne equivalent amount of hydrogen, and the heat of combustion of the compound was then taken to be equal to the heats of combustion of the elements in the residue. That the rule is not very accurate may be seen from the following example. Cane-sugar has the formula C12HnOn. According to Welter’s rule, we deduct 11 O with the equivalent amount of hydrogen, namely, 22 H, and are left with the residue 12 C, the heat of combustion of which is 1131600 cal. The observed heat of combustion of sugar is, however, 1354000, so that the error of the rule is here 20 per cent. A much better approximation to the heat of combustion of such substances is obtained by deducting the oxygen together with the amount of carbon necessary to form CO2, and then ascertaining the amount of heat produced by the residual carbon and hydrogen. In the above case wc should deduct with 11 O the equivalent amount of carbon 5∙5 C, thus obtaining the residue 6∙5 C and 22 H. These when burnt would yield (6∙5×94300) + (ι 1 ×68300) = 1364250 cal., an amount which is less than 1 per cent, different from the observed heat of combustion of sugar. Neither of the above rules can be applied to carbon compounds containing nitrogen.

§ 8. *Heat of Neutralization.—*It has already been stated that the heats of neutralization of acids and bases in aqueous solution are additively composed of two terms, one being constant for a given base, the other constant for a given acid. In addition to this, the further regularity has been observed that when the powerful monobasic acids are neutralized by the powerful monacid bases, the heat of neutralization is in all cases the same. The following table gives the heats of neutralization of the commoner strong monobasic acids with soda:—

Hydrochloric acid . HCl . . . 137400 cal.

Hydrobromic acid . HBr . . 1375θθ »

Hydriodic acid . . HI . . . 136800 „

Nitric acid . . HNO3 . . 136800 „

Chloric acid HC103 . 137600 ,,

Bromic acid HBrO3 . 137800 ,,

Within the error of experiment these numbers are identical.

It was at one time thought that the greater the heat of neutralization of an acid with a given base, the greater was the strength of the acid. It is now known, however, that when weak acids or bases are used, the heat of neutralization may be either greater or less than the normal value for powerful acids and bases, so that there is no proportionality, or even parallelism, between the strengths of acids and their heats of neutralization (see Solutions).

§ 9. *Heat of Solution.—*When substances readily combine with water to form hydrates, the heat of solution in water is usually positive; when, on the other hand, they do not readily form hydrates, or when they are already hydrated, the heat of solution is usually negative. The following examples show the effect of hydration on heat of solution in a large quantity of water:—

Heat oí Solution. Heat oí Hydration.

I. Sodium carbonate—

Na3CO3 . . . +5640 cal.

Na3CO3, H2O . +2250 „ +3390 cal.

. Na3CO3, 2H2O . +20 ,, +5620 ,,

Na3CO3, ιoII2O —16160 ,, +21800 „

II. Sodium sulphate—

Na2SO3 . . +460 cal.

Na2SC)4, II2O —1900 „ +2360 cal.

Na2SO<, ioH2O . —18760 „ +19200 „

§ 10. *Application of the Second Law of Thermodynamics to Thermochemistry.—*What is commonly understood by thermo­chemistry is based entirely on the first law of thermodynamics, but of recent years great progress has been made in the study of chemical equilibrium by the application of the second law. For an account of work in this direction see Chemical Action.

Bibliography.—Julius Thomsen, *Thermochemische Untersuch­ungen* (Leipzig, 1882-86); Μ. Berthelot, *Essai de Mécanique Chimique fondée sur la Thermochimie* (Paris, 1879); *Thermochimie, données et lois numériques* (Paris, 1897); W. Ostwald, *Lehrbuch der allgemeinen Chemie,* 2nd cd., vol. iι. part 1, pp. 1-517 (Leipzig, 1893); Μ. Μ. P. Muir and D. Μ. Wilson, *Elements of Thermal Chemistry* (London, 1885); P. Duhem, *Traité de Mécanique Chimique* (Paris, 1897-99); J. J. van Laar, *Lehrbuch der mathematischen Chemie* (Leipzig, 1901). (J. Wal.)

**THERMODYNAMICS** (from Gr. *θepμbs,* hot, *δυvaμιs,* force).

1. The name thermodynamics is given to that branch of the general science of Energetics which deals with the relations between thermal and mechanical energy, and the transforma­tions of heat into work, and vice versa. Other transformations of heat are often included under the same title (see Energetics). An historical account of the development of thermodynamics is given in the article Heat. The object of the present article is to illustrate the practical application of the two general principles— (1) Joule’s law of the equivalence of heat and work, and (2) Carnot’s principle, that the efficiency of a reversible engine depends only on the temperatures between which it works; these principles are commonly known as the first and second laws of thermodynamics. The application will necessarily be confined to simple cases such as are commonly met with in practice, or are required for reference in cognate subjects.

2. *Application of the First Law.—*The complete transforma­tion of mechanical energy into heat by friction, or some analogous process of degradation, is always possible, and is made the basis of experiments for the determination of the mechanical equi­valent of the heat unit (see Calorimetry). The converse pro­cess of the transformation of heat into mechanical work or other forms of energy is subject to limitations.

When a quantity of heat, *II,* is supplied to a body, part is expended in raising the temperature of the body, or in expanding the volume against molecular forces, and is represented by an increase in the total quantity of energy contained in the body, which is generally called its *Intrinsic Energy,* and will be denoted by the symbol E. The remainder is equivalent to the external work, *W,* done *by* the body in expanding or otherwise, which can be utilized for mechanical purposes, and ceases to exist as heat in the body. The application of the first law leads immediately to the equation,

*II≈E-Eo+W,* (ι)

in which Eα represents the quantity of energy originally present in the body, and all the quantities are supposed, as usual, to be expressed in mechanical units. This equation is generally true for any series of transformations, provided that we regard *II* and *W* as representing the *algebraic sums* of all the quantities of heat supplied to, and of work done *by* the body, heat taken *from* the body or work done *on* the body being reckoned negative in the summation. *E— Eo,* then, represents the total increase of the intrinsic energy of the body in its final state, which may be deter­mined by measuring *II* and *W.* If after any series or cycle of transformations the body is restored to its initial state, we must have E = Eo, whence it follows that *II=W.* But this simple rela­tion is only true of the net balances of heat and work in a complete cyclical process, which must be adopted for theoretical purposes if we wish to eliminate the unknown changes of intrinsic energy. The balance of work obtainable in such a cycle depends on the limits of temperature in a manner which forms the subject of the second law.

3. *Indicator or p.υ. Diagram.—*The significance of relation (1) is best appreciated by considering the graphic representation of quantities of heat and energy on a work-diagram.

On the familiar indicator diagram the state of the working sub­stance is represented by the position of a point called the “ state­point,” defined by the values of the pressure *p* and volume *v of unit mass,* as ordinate and abscissa respectively (fig. l)1 Any line (“ path ” or “ graph ”) on the diagram, such as BCD, represents an “ operation ’ or “ process ” *i.e.* a continuous series of states through which the substance may be made to pass in any trans­formation. It is tacitly assumed that the motion is relatively so slow that the pressure and temperature of the substance are prac­tically uniform throughout its mass at any stage of the process. Otherwise the transformation could not be fully represented on the diagram, and would not be reversible. The area BCDd⅛ under the path represents the external work done *by* the substance in