

XX.—*Investigations of the Specific Heat of Solid Bodies.*

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I. *Historical Introduction.*

1. ABOUT the year 1780 it was distinctly proved that the same weights of different bodies require unequal quantities of heat to raise them through the same temperature, or give out unequal quantities of heat on cooling through the same number of thermometric degrees. It was recognised that for different bodies the unequal quantities of heat, by which the same weights of different bodies are heated through the same range, must be determined as special constants, and considered as characteristic of the individual bodies. This newly discovered property of bodies, Wilke designated as their *specific heat*, while Crawford described it as the *comparative heat*, or as the *capacity of bodies for heat*. I will not enter upon the earliest investigations of Black, Irvine, Crawford, and Wilke, with reference to which it may merely be mentioned that they depend essentially on the thermal action produced when bodies of different temperatures are mixed, and that Irvine appears to have been the first to state definitely and correctly in what manner this thermal action (that is, the temperature resulting from the mixture) depends on the original temperature, the weights, and the specific heats of the bodies used for the mixture. Lavoisier and Laplace soon introduced the use of the ice-calorimeter as a method for determining the specific heat of bodies: and J. T. Mayer showed subsequently that this determination can be based on the observation of the times in which different bodies placed under comparable conditions cool to the same extent by radiation. The knowledge of the specific heats of solid and liquid bodies gained during the last century, and in the first sixteen years of the present one, by these various methods, may be left unmentioned. The individual determinations then made were not sufficiently accurate to be compared with the present ones, nor was any general conclusion drawn with reference to the specific heats of the various bodies.

2. Dulong and Petit's investigations, the publication of which commenced in 1818, brought into the field more accurate deter-

	Berzelius's atomic weights.	Regnault's thermal atomic weights.	Usual equivalent weights.	Modern atomic weights.
Aluminium ..	Al = 13·7	Al = 13·7	Al = 13·7	Al = 27·4
Antimony ....	Sb = 61	Sb = 61	Sb = 122	Sb = 122
Arsenic .....	As = 37·5	As = 37·5	As = 75	As = 75
Barium .....	Ba = 68·5	Ba = 68·5	Ba = 68·5	Ba = 137
Bismuth .....	Bi = 105	Bi = 105	Bi = 210	Bi = 210
Boron .....	B = 10·9	B = 10·9	B = 10·9	B = 10·9
Bromine .....	Br = 40	Br = 40	Br = 80	Br = 80
Cadmium .....	Cd = 56	Cd = 56	Cd = 56	Cd = 112
Calcium .....	Ca = 20	Ca = 20	Ca = 20	Ca = 40
Carbon .....	C = 6	C = 12	C = 6	C = 12
Chlorine .....	Cl = 17·75	Cl = 17·75	Cl = 35·5	Cl = 35·5
Chromium .....	Cr = 26·1	Cr = 26·1	Cr = 26·1	Cr = 52·2
Cobalt .....	Co = 29·4	Co = 29·4	Co = 29·4	Co = 58·8
Copper .....	Cu = 31·7	Cu = 31·7	Cu = 31·7	Cu = 63·4
Fluorine .....	Fl = 9·5	Fl = 9·5	Fl = 19	Fl = 19
Gold .....	Au = 98·5	Au = 98·5	Au = 197	Au = 197
Hydrogen .....	H = 0·5	H = 1	H = 1	H = 1
Iodine .....	I = 63·5	I = 63·5	I = 127	I = 127
Iridium .....	Ir = 99	Ir = 99	Ir = 99	Ir = 198
Iron .....	Fe = 28	Fe = 28	Fe = 28	Fe = 56
Lead .....	Pb = 103·5	Pb = 103·5	Pb = 103·5	Pb = 207
Lithium .....	Li = 7	Li = 3·5	Li = 7	Li = 7
Magnesium ..	Mg = 12	Mg = 12	Mg = 12	Mg = 24
Manganese ..	Mn = 27·5	Mn = 27·5	Mn = 27·5	Mn = 55
Mercury .....	Hg = 100	Hg = 100	Hg = 100	Hg = 200
Molybdenum ..	Mo = 48	Mo = 48	Mo = 48	Mo = 96
Nickel .....	Ni = 29·4	Ni = 29·4	Ni = 29·4	Ni = 58·8
Nitrogen .....	N = 7	N = 7	N = 14	N = 14
Osmium .....	Os = 99·6	Os = 99·6	Os = 99·6	Os = 199·2
Oxygen .....	O = 8	O = 8	O = 8	O = 16
Palladium .....	Pd = 53·3	Pd = 53·3	Pd = 53·3	Pd = 106·6
Phosphorus ..	P = 15·5	P = 15·5	P = 31	P = 31
Platinum .....	Pt = 98·7	Pt = 98·7	Pt = 98·7	Pt = 197·4
Potassium .....	K = 39·1	K = 19·55	K = 39·1	K = 39·1
Rhodium .....	Rh = 52·2	Rh = 52·2	Rh = 52·2	Rh = 104·4
Rubidium .....	Rb = 85·4	Rb = 85·4	Rb = 85·4	Rb = 85·4
Selenium .....	Se = 39·7	Se = 39·7	Se = 39·7	Se = 79·4
Silicium .....	Si = 21	Si = 14	Si = 14	Si = 28
Silver .....	Ag = 108	Ag = 54	Ag = 108	Ag = 108
Sodium .....	Na = 23	Na = 11·5	Na = 23	Na = 23
Strontium .....	Sr = 43·8	Sr = 43·8	Sr = 43·8	Sr = 87·6
Sulphur .....	S = 16	S = 16	S = 16	S = 32
Tellurium .....	Te = 64	Te = 64	Te = 64	Te = 128
Thallium .....	Tl = 204	Tl = 102	Tl = 204	Tl = 204
Tin .....	Sn = 59	Sn = 59	Sn = 59	Sn = 118
Titanium .....	Ti = 25	Ti = 25	Ti = 25	Ti = 50
Tungsten .....	W = 92	W = 92	W = 92	W = 184
Zinc .....	Zn = 32·6	Zn = 32·6	Zn = 32·6	Zn = 65·2
Zirconium .....	Zr = 33·6	Zr = 33·6	Zr = 44·8	Zr = 89·6

minations, and a general law. The investigations of the relations between the specific heats of the elements and their atomic weights date from this time, and were afterwards followed by similar investigations into the relations of the specific heats of compound bodies to their composition. In order to give a general view of the results of these investigations, it is desirable to present, for the elements mentioned in the sequel, a synopsis of the atomic weights assumed at different times, and of certain numbers which stand in the closest connexion with these atomic weights.

For each of the previous columns, the relation of the numbers to each other is alone important, and not the number which is taken as unit or starting-point. Berzelius's atomic weights and Regnault's thermal atomic weights are corrected with the nearest and most trustworthy experimental determinations, without alteration of the bases for the adoption of these numbers. The numerical relations presented in the above Table require, from the chemical point of view, no further explanation. The relations of these numbers to the specific heat form the subject of the investigations which are presented in the sequel.

3. The experiments by which Dulong and Petit\* showed, in the case of mercury, various solid metals, and glass, that the specific heat increases with increasing temperature, were made by the method of mixtures. They determined at ordinary temperatures the specific heats of a greater number of elements by the method of cooling.† They found that when the numbers in the first column in § 2 corresponding to the elements Bi, Pb, Au, Pt, Sn, Zn, Cu, Ni, Fe, and S (the Berzelian atomic weights) are multiplied by the respective specific heats of these bodies, approximately the same number is obtained; and that approximately the same number is also obtained when  $\frac{1}{2}$  Ag,  $\frac{1}{2}$  Te, and  $\frac{2}{3}$  Co are multiplied by their corresponding specific heats. They were of opinion that the atomic weights of the elements could and should be so selected that, when multiplied by the specific heats, they should give approximately the same number as product. This observation and this view, which Dulong and Petit stated in 1819 in the following manner, "The atoms of all simple bodies have all exactly the same capacity for heat," have since that time been known as Dulong and Petit's Law.

I shall not here dwell upon Potter's investigations on the specific heat of metals and on the validity of Dulong and Petit's

\* Ann. Ch. Phys. [2], vii, 142.

† Ibid. x, 395.

law,\* but proceed directly to discuss Neumann's investigations, which rank worthily by the side of those of Dulong and Petit.

4. In his "Investigation on the specific heat of Minerals," Neumann (in 1831) first published† more accurate determinations of the specific heats of solid compounds. He investigated a large number of such compounds, especially those occurring in nature, partly by the method of mixture, and partly by the method of cooling; and he determined the sources of error in both these methods, and the corrections necessary to be introduced. In a postscript of this paper, he mentioned that he continued the investigations with an apparatus which, compared with that he had previously used, promised far greater accuracy in the individual results, without needing tedious and troublesome reductions. This apparatus, by means of which the specific heats of solid bodies, which may be heated in a closed space surrounded by steam, can be determined with great accuracy, he has not described.‡

Of the general results of Neumann's investigations, one must be particularly mentioned, that a dimorphous substance has the same specific heat in its two conditions. This he showed was the case with arragonite and calcite, and with iron pyrites and marcasite. But the most important is the discovery that in analogous compounds the products of the atomic weights into the specific heats are approximately equal. Neumann stated this last observation in the following manner:—"In bodies of analogous chemical composition the specific heats are inversely as the stoichiometrical quantities, or, what is the same, stoichiometrical quantities of bodies of analogous chemical composition have the same specific capacity for heat." Neumann adduced 8 carbonates, 4 sulphates, 4 sulphides (MeS), 5 oxides (MeO), and 3 oxides (Me<sub>2</sub>O<sub>3</sub>), as showing this regularity, which is to be denoted as Neumann's law.§

\* Edinburgh Journal of Science, new series, vol. v, p. 75, and vol. vi, p. 166. J. F. W. Johnston's remarks, vol. v, p. 278. I know these papers only from Berzelius's Jahresbericht, vol. xii, p. 17, and Gehler's Physicalisches Wörterbuch, new edition, vol. x, part 1, p. 805, *et seq.*

† Pogg. Ann. xxiii, 1.

‡ Pape (Pogg. Ann. cxx, 337) has recently described this apparatus. I have had no opportunity of seeing Neumann's memoir cited by Pape, "Commentatio de emendanda formula per quam calores corporum specifici ex experimentis methodo mixtionis institutis computantur." Regiomonti, 1834.

§ The objection of Regnault (Ann. Ch. Phys. [3], i, 131) as to the inadequacy of the proofs adduced by Neumann in support of the law are not conclusive.

5. Soon after the publication of Neumann's researches in 1833, Avogadro published\* a "Memoir on the Specific Heat of Solid and Liquid Bodies." He there gave a number of determinations of the specific heat of solid bodies made by the method of mixture. As far as can be ascertained by comparison with the most trustworthy of our newer determinations, these results are by no means so accurate as those of Neumann; but they are far more accurate than those which had been obtained up to about 1830, and many of them come very close to the best of our modern results. It would be unjust to Avogadro's determinations† to judge them all by one case, in which he obtained a totally erroneous result (for ice, by a modified method); and by the circumstance that in a subsequent memoir‡ he gives specific heats for several elements, as deduced from his experiments, which are decidedly incorrect.§ Avogadro recognizes the validity of Dulong and Petit's law. With reference to the specific heats of compound bodies, he considers that he had established, with tolerable probability, that for solid and liquid bodies, the same regularity prevails that he had previously deduced for gases from Dulong's experiments. That is, "that the specific heat of the atom of a compound body is equal to the square root of the integral or fractional number expressing the atoms or parts of atoms which go to form the atom of the compound body, such as it exists in the solid or liquid state, taking as unity the specific heat of the atom of a simple body in the same state." He observes that there is a difficulty incidental to the application of this law to solid and liquid bodies, which is not met with in the case of gaseous bodies, in which the composition by atoms or by volumes is held to be directly given by observation. This difficulty consists in knowing what constitution is to be assigned to the body in question for the solid or liquid condition; this constitution, from the conclusions derived from his theoretical considerations, would often be different from that which the body has

\* Ann. Ch. Phys. [2] lv. 80, as an abstract from *Memorie della Società Italiana delle Scienze residente in Modena*, t. xx. Fascicolo 3 di fisica.

† They are also found in Gmelin's *Handbuch der Chemie*, 4 Auflage, vol. i. in the Tables, pp. 215-218 *et. seq.* (English Edition I, 241-244 *et. seq.*)

‡ Ann. Ch. Phys. [2] vol. lvii. p. 113.

§ I know Avogadro's investigations only from the abstracts published in the *Annales de Chimie et de Physique*, and am not aware whether the bold corrections of Avogadro urged by Regnault (*Ann. Ch. Phys.* [2] lxxiii, 10) were used in all his experiments, or only in some.

in the state of gas or vapour. His considerations led him to assume the atomic weights of many elements different from those which Berzelius had given: Avogadro described the atoms, to which the weights assumed by him refer, as *thermal atoms*.

6. R. Hermann published in 1834 a memoir "On the proportions in which Heat unites with the Chemical Elements and their Compounds, and on the Combining Weights considered as quotients of the capacity for Heat of Bodies into their Specific Gravities"\*. He gives there a great number of determinations of the specific heat of solid bodies (of a few elements, but chiefly of compound bodies). He made a few experiments in which he used Lavoisier and Laplace's calorimeter†; but by far the greater number of determinations are made by the method of cooling.‡ Many of his results approach very closely to those which are at present considered accurate, but a considerable number among them are decidedly incorrect.

As for Hermann's theoretical results, it must be borne in mind that, regarding matter as he does, not from the point of view of the atomic, but of the dynamical theory, he puts the idea of combination-weights in the place of the idea of atomic weights. The propositions which he endeavours to establish are the following:—The quotients obtained by dividing the specific gravities of the elements§ in the solid state by their specific gravities in the gaseous state, are either equal or stand to each other in simple ratios; they are 1, 2, . . . . 15 times as much as a certain base. The same is the case with the products of the specific gravities of the solid elements into their specific heats, that is, with their relative heat; and the number indicating the multiple for a given element is the same for both the above relations. It follows from this that the combining weights  $m$  of the elements are proportional to the quotients of their relative heats into their specific gravities in the solid condition; that the products of the specific heats and

\* *Nouveaux Mémoires de la Société Impériale des Naturalistes de Moscou*, vol. iii p. 137.

† Hermann tried to alter this apparatus so as to make it serve for measuring the change of volume which takes place when ice melts; but he did not further follow this application of the modified apparatus.

‡ They are found not quite complete in Gmelin's *Handbuch der Chemie*, 4 Auflage, in the Tables. pp. 215-218 *et. seq.* (English edition I, 241-244 *et. seq.*)

§ Hermann considers that the specific gravities of the elements in the state of gas or vapour are either obtained by observation, or may be theoretically deduced by assuming that they are in the ratio of the combining weights.

the combining weights for different elements are equal to a constant, and that from the known combining weight of an element its specific heat in the solid form may be calculated (it is equal to  $\frac{0.375}{m}$ , where  $m$  is the combining weight of the substance in question referred to oxygen = 1). For several elements (phosphorus, tellurium, cadmium, and silver for instance) atomic weights are taken which differ from those of Berzelius. In the case of the sulphides, the specific heats may be calculated from those of the constituents, assuming that the specific heats of the elements in these compounds are the same as in the free state. The same holds good for several chlorides and for basic metallic oxides, if the specific heats of chlorine and of oxygen, as given by the above formula, are taken as basis. But in acids a smaller specific heat must be taken for oxygen (one-half in several acids and null in phosphoric acid); and there are even compounds (cassiterite, *e.g.*, or arsenious acid), in which the same element is contained partly with the normal and partly with the modified specific heat\*. For oxygen-salts it is to be assumed that both the acid and the base have the same specific heat as in the free state, and hence the specific heat of one constituent (of the acid, for instance) may be calculated, if that of the salt and that of the other constituent (the base) is known; and it is also found that the specific heat of chromic acid in neutral and in acid chromate of lead is the same.

This memoir of Hermann's did not become much known. Unacquainted with it, other philosophers have subsequently developed independently similar opinions.

7. In 1835 Rudberg described a method,† which, by ascertaining the heat developed when salts are dissolved in water, in experiments in which the proportion of the salt to the water was constant, but the temperature of the salt varied, should give a means of at once determining the specific heat of the salt, and of the heat which was either absorbed or became free. Yet the numbers which he obtained from his experiments for the specific heat of solid salts are undoubtedly erroneous.

\* Hermann designates such compounds as hermaphrodites. He thinks that an acid and a base may have the same composition, and that they may form salts with each other. Cassiterite, for instance, he considers to be stannate of binoxide of tin.

† Berzelius's Jahresbericht, vol. xv, p. 63. Pogg. Ann. xxxv, 474.



Dumas\* (in 1838) discussed the possibility of determining the specific heat of organic bodies by the following process. A platinum vessel containing the substance in question, along with a thermometer, is to be heated to 30° or 40°, and then brought into a vessel provided with a second thermometer, and containing water, the temperature being about 5° or 6° lower than that of the surrounding room. When the temperature has risen to the same extent above that of the room, both thermometers are to be observed. I know no determinations made by this method.

8. In 1840 Regnault commenced the publication of a series of important investigations which he had made on specific heat. As they are generally known, I may be more brief in enumerating the contents of the individual publications. In the first which he published, Regnault developed‡ the reasons which led him to prefer the method of mixture to other processes for determining the specific heats of solid bodies; he described his mode of executing this method, and published the results obtained for a great number of elements. In a second memoir‡ he gave the specific heats of several metallic alloys containing metals in simple atomic ratios, and of a great number of solid chemical compounds; and he published comprehensive experiments on the specific heat of carbon in its different conditions. The investigations announced in the first memoir§ on the specific heat of organic compounds, as well as those promised in the second memoir|| on the specific heat of sulphur at different temperatures, have not to my knowledge been published. But in a third memoir¶ Regnault has investigated the difference in the specific heats of certain metals, according as they are hardened or soft, and also with reference to sulphur according as it is in the native crystallised form, or has solidified a longer or shorter time after being melted; and he has more especially tried to impart greater certainty to the method of cooling. In his subsequent investigations, however, he has used only the method of mixture as being the more certain. These investigations\*\* have given the specific heats of a large number of solid elements, and also of individual compounds.

\* Dumas's Thèse sur la question de l'action du calorique sur les corps organiques (Paris, 1838), Ann. Ch. Pharm. xxviii, 151.

† Ann. Ch. Phys. [2] lxxiii, 5.

‡ Ann. Ch. Phys. [3] i, 129.

§ Ibid. [2] lxxiii, 71.

|| Ibid. [3] i, 205.

¶ Ibid. [3] ix, 322.

\*\* Ibid. [3] xxvi, 261 & 268; xxxviii, 129; xlvi, 257; lxiii, 5. Compt. rend. lv, 887.



By his investigations Regnault has removed some objections which seemed to affect Dulong and Petit's law, and has given a great number of new cases in which it applies. He considers\* this law to be universally valid, and discusses the reasons why for individual elements the specific heats found do not quite agree with the law, but only approximately. In his view the atomic weight of an element is to be so taken that it agrees with Dulong and Petit's law. He took the atomic weight of silver and of the alkaline metals half as great, and that of carbon twice as great as Berzelius had done. Yet with regard to selecting, by means of the specific heat, from among the numbers which the chemical investigations of an element has given as admissible, that which is the correct one, Regnault does not always express himself decidedly. In the case of carbon† and of silicium‡ he mentions the possibility of their disagreement with Dulong and Petit's law. He proved the validity of Neumann's law for a number of cases very considerably greater than that on which it had originally been based, and he expressed it in a much more general form.§ "In all compounds of analogous atomic composition, and similar chemical constitution, the specific heats are approximately inversely proportional to the atomic weights. Regnault designates the numbers agreeing with this law as thermal atomic weights. He has either determined them directly from the numbers found for the specific heats of the elements in the free state, applying Dulong and Petit's law, or indirectly by ascertaining the specific heat of solid compounds, assuming Neumann's law; or finally (and only in a few cases), he has determined them by means of their probable analogies. These are the atomic weights given in the second column of the table in § 2.

With regard to the relations of the specific heats of solid compounds to those of their constituents, Regnault has shown|| that with metallic alloys, at a considerable distance from their melting points, the specific heats may be calculated from those of their constituents in tolerable accordance with the experimental results, assuming that the specific heats of the metals are the same in the alloys as in the free state. The investigation, whether for true

\* Ann. Ch. Phys. [2] lxxiii, 66; further, [3] xxvi, 261, and xlvi, 257.

† Ibid. [3] i, 205. But both before and after (Ibid. [2] lxxiii, 71. and [3] xxvi, 263) Regnault inclined to the view that carbon, with the equivalent=12, and the specific heat found for wood-charcoal, must be considered as obeying Dulong and Petit's law.

‡ Ibid. lxxiii, 30.

§ Ibid. i, 199.

|| Ann. Ch. Phys. [3] i, 183.

chemical compounds there is a simple relation between their specific heats and those of their constituent elements, Regnault has reserved\* till the conclusion of his experiments on the specific heats of gaseous bodies.† To my knowledge he has published nothing for solid bodies. But in 1862, with reference to the relations which had been recognized between the specific heats and atomic weights of solid, simple, or compound bodies, he spoke as follows.‡ “It is true that these laws, in the case of solid bodies, apply only approximately to simple bodies and those compounds of least complex constitution; for all others it is impossible to pronounce anything in this respect.” From some remarks of Regnault with reference to carbon§ and silicium,|| he considers it possible, or probable, that the specific heat of certain elements in their compounds is different from that which they possess in the free state.

9. In 1840 De la Rive and Marcet published¶ investigations on the specific heat of solid bodies. They made their determinations by the method of cooling. They found that, assuming Berzelius’s atomic weights, selenium, molybdenum, and wolfram fall under Dulong and Petit’s law, which they consider as universally valid; but that carbon forms an exception, and they consider it as probable that its true atomic weight has not yet been ascertained. For several sulphides they found a greater specific heat than was calculated for them, assuming that their constituents have in them the same specific heat as in the free state. They think that for solid as well as for liquid and gaseous compounds, the law governing the specific heat is still unknown. A subsequent memoir by these physicists\*\* treated of the specific heat of carbon in its various conditions.

10. In 1840†† H. Schröder made an investigation as to what volumes are to be assigned to the constituents of solid and liquid compounds when contained in those compounds. In his memoirs on the subject, he expressed the view that the specific heat of compounds depends on the specific heats of the constituents in

\* Ibid. p. 132.

† Regnault has made known the results of these experiments in 1853 by a preliminary account in the *Comptes Rendus*, vol. xxxvi, p. 676, and more completely in 1862 in his “*Relation des expériences pour déterminer les lois et les données physiques nécessaires au calcul des machines à feu*,” vol. ii, p. 3.

‡ *Relation, &c.*, vol. ii, p. 289.

|| Ibid. [3] lxiii, 31.

\*\* Ibid. [3] ii, 121.

§ *Ann. Ch. Phys.* [3] i, 205.

¶ Ibid. [2] lxxv, 113.

†† *Pogg. Ann.* 1, 553.

that particular state of condensation in which they are contained in the compounds in question. In 1841\*, reasoning from the results of Regnault's experiments, he endeavoured to show that the atomic heat (that is the product of the atomic weight into the specific heat) of a compound is equal to the sum of the atomic heats for the states of condensation in which the elements are contained in the compound, and to ascertain what atomic heats are to be assigned to certain elements in certain compounds. On the assumption that the atomic heat of metals in compounds is as great as in the free state, he endeavoured to determine the atomic heat of oxygen, sulphur, &c., in certain compounds of these elements with the metals; he came to the conclusion that an element (sulphur for instance) may in some compounds have an atomic heat different from that which it has in the free state; and the same element (sulphur or oxygen for instance) may have different atomic heats in different compounds; but the changes in the atomic heat of an element always ensue in simple ratios. I cannot here adduce the individual results which he obtained when he inferred the atomic heat of an element in a compound by subtracting from the atomic heat of the compound the atomic heat of the other elements in it, which he had calculated either from direct determinations of their specific heat, or from previous considerations. The essential part of Schröder's conception is that in this manner the atomic heat of a body, as a constituent of a compound, may be indirectly determined; and the result is that the atomic heat, at any rate of some elements in compounds, is different from what it is in the free state, and may be different in different compounds, and that the changes are in simple ratios. Schröder considered also that there was probably a connexion between these changes and those of the volumes of the elements, without, however, stating how the one change might be deduced from the other.

11. L. Gmelin (in 1843)† considered it as inadmissible, from the chemical point of view, to assign throughout such atomic weights to the elements as to make them agree with Dulong and Petit's law. Certain exceptions must be admitted. Comparing the specific heats of oxygen, hydrogen, and nitrogen for the gaseous state with the specific heats of other elements in the solid

\* Pogg. Ann. lii, 269.

† L. Gmelin's *Handbuch der Chemie*, 4th ed. vol. i, p. 217. (English edition, i, 243.)

state, he came to the conclusion that if the numbers given in § 2 as the equivalents ordinarily assumed be taken as atomic weights, the atomic heat of hydrogen, of nitrogen, and by far the greater number of the elements is equal to about 3·2; several of them twice as great; that of oxygen one-half; that of carbon (as diamond) one-fourth as great. With reference to the dependence of the atomic heats of the compounds on those of the elements, Gmelin expressed the opinion\* that in general the elements, on entering into compounds, retain the atomic heats they have in the free state; but for individual elements, especially for oxygen and carbon, it must be assumed that their atomic heat changes in simple ratios with the compounds into which they enter.

12. Wæstyn was also of opinion† that the specific heats of the elements remain unchanged when they enter into chemical compounds. In 1848 he stated as a general proposition: "The quantity of heat necessary to raise the temperature of the atomic weight of a body through 1° is equal to the sum of the quantities of heat necessary to raise the temperature of the atoms, and fractions of atoms, through 1°." If  $A$  is the atomic weight and  $C$  the specific heat of a compound,  $a_1, a_2, a_3 \dots$  the atomic weights‡, and  $c_1, c_2, c_3 \dots$  the specific heats of the elements contained in it, and  $n_1, n_2, n_3 \dots$  the numbers which express how many atoms of each element are contained in an atom of the compound, then

$$AC = n_1 a_1 c_1 + n_2 a_2 c_2 + n_3 a_3 c_3 \dots$$

As a proof of this law, he compared the calculated values of  $AC$  of several compounds (metallic iodides and sulphides) and alloys with the observed values, taking Regnault's determinations of the specific heats of the elements and of the compounds. It follows, further, from that proposition, that if the formula and the values for several compounds are compared with each other, there must be the same differences of the values  $AC$  for the same differences of formulæ. Wæstyn showed by a number of examples that this is so approximately. By means of this law, the product of the specific heat and the atomic weight for one constituent of a compound may be found, if this is known for the compound and the other constituents. Wæstyn deduced in this way the product

\* Ibid. p. 222: compare an earlier remark of Gmelin which applies to this subject (1840) in the new edition of Gehler's *Physikalisches Wörterbuch*, vol. ix, p. 1941:

† *Ann. Ch. Phys.* [3] xxiii, 295.

‡ Wæstyn based his considerations on Regnault's thermal atomic weights.

for oxygen (by subtracting from the product for different metallic oxides that found for the metals, and from chlorate of potassium, that for chloride of potassium) to be 2·4 to 2·1 (O.=8), and for chlorine 3·0 to 3·5 (Cl.=17·75). Wæstyn finally expressed a doubt whether Neumann's law is universally applicable. He laid stress on the circumstance that when two elements gave different products, the difference is also met with in the products for their analogous compounds; and, for instance, the greater products which mercury and bismuth have in comparison with other elements, are also met with in the compounds of these metals.

13. Garnier (in 1852) developed the view\*, that not only in the case of elements are the atomic weights  $A$  † inversely proportional to the specific heats  $C$ , but that the same is the case with water and solid compounds in whose atom  $n$  elementary atoms are contained, if the so-called mean atomic weight  $\frac{A}{n}$  be compared with the specific heat  $C$ ; for elements  $A \times C = 3$ , and for compound bodies  $\frac{A}{n} \times C = 3$  (if O=8). He endeavoured to prove this from Regnault's determinations of specific heats. From the latter equation he calculated the specific heat for several compounds. In the case of the basic oxides, sulphides, chlorides, bromides, and iodides, his calculated results agree tolerably with the observed ones; this is less the case with metallic acids and oxygen-salts, for which calculation mostly gives results far too large. Garnier ‡ drew, further, from the above proposition, the conclusion that the atomic weight of hydrogen, chlorine, &c., must in fact be taken only half as great as the respective equivalent weights; for only by assuming this smaller atomic weight is the mean atomic weight such that its product with the specific heat is near 3.

In 1852 Bancalari § repeated that the specific heat of an atom of a compound body (that is, its atomic heat) is equal to the sum of the specific heats of the individual constituent simple atoms, and showed, from a series of examples (oxides, chlorides, sulphates, and nitrates), that, according to that proposition, the

\* Compt. Rend. xxxv, 278.

† If Regnault's thermal atomic weights are taken.

‡ Compt. Rend. xxxvii, 130.

§ An abstract from Memorie della Accademia delle Scienze di Torino [2], vol. xiii, p. 287, in the Archives des Sciences Physiques et Naturelles, vol. xxii, p. 81. I know the contents of this memoir only from this abstract.

atomic heats of many compounds may be calculated in tolerable approximation with those derived from Regnault's experimental investigations, if, for the elements which he investigated, the atomic heats derived from his determinations be taken as a basis, that is, for oxygen ( $O=8$ ) the atomic heat 1.89; for chlorine ( $Cl=17.73$ ) 3.21; for nitrogen ( $N=7$ ) 3.11.

Cannizaro (in 1858\*) has used the proposition, that, in the sense above taken, universally  $\frac{AC}{n} = \text{a constant}$ , for the purpose of ascertaining the value of  $n$  for the atomic weight of different compounds, and therewith ascertaining the atomic weight of elements which are contained in these compounds.

14. Besides those of Regnault, but few experimental determinations of the specific heats of solid bodies have been published. Bede† and Byström‡ have published investigations on the specific heat of several metals at different temperatures §: both sets of experiments were made by the method of mixtures. From the year 1845, Person||, in his investigations on the specific heat of ice, then on the latent heats of fusion, and their relations to the specific heats in the solid and liquid state has determined the specific heat for several solid substances, especially also for some hydrated salts. He worked more especially by the method of mixture. He observed ¶, in the case of these salts, that their specific heats may be calculated in close approximation with those found experimentally on the assumption that the constituents, anhydrous salt and water considered as ice, have the same specific

\* Il Nuovo Cimento, vol. vii, p. 321. Piazza also gives a statement of this speculation in his pamphlet "Formole atomistiche e tipi chimici," 1863. I know this only from a notice in the Bulletin de la Société Chimique de Paris, 1863.

† An abstract from the Bulletin de l'Académie des Sciences de Belgique, vol. xxii, p. 473, and the Mémoires Couronnés par l'Académie de Belgique, vol. xxvii, appeared in the Bericht über die Fortschritte der Physik im Jahre 1855, dargestellt von der physikalischen Gesellschaft zu Berlin, p. 379.

‡ Abstract from the Oversigt of Stockholm Vetenskaps-Akademiens Förhandlingar, 1860, in the same Jahresbericht, 1800, p. 369.

§ To the experiments of Dulong and Petit on this subject, mentioned in § 3, Pouillet's determinations of the specific heat of platinum at different temperatures must be added (Compt. Rend. ii, 782).

|| Compt. Rend. xx, 1457; xxiii, 162 and 366. Ann. Ch. Phys. [3], xxi, 295; xxiv, 129; xxvii, 250; xxx, 78.

¶ Person expressed this in 1845 (Compt. Rend. xx, 1457), with regard to his determinations of the specific heat of crystallised borax and of ordinary phosphate of soda. He has subsequently published the results of his experiments for the latter salt (Ann. Ch. Phys. [3], xxvii, 253), but I cannot find the number which he found for crystallised borax.

heats in them as in the free state. By the same method, Alluard\* (in 1859) determined the specific heat of naphthalene. Schafarik †, lastly, has executed, by the method of mixtures, a series of experiments on the determination of the specific heats of vanadic, molybdic, and arsenious acids.

Quite recently (1863), Pape ‡ has published investigations on the specific heat of anhydrous and hydrated sulphates. He worked by the method of mixture, which he modified in the case of salts rich in water, by placing them in turpentine, and observing the increase of temperature produced in the salt and in the liquid by immersing heated copper. As a more general result, Pape finds that for hydrated sulphates of analogous formulæ, the products of the specific heats and the equivalents are approximately equal; and further, that with sulphates containing different quantities of water, the product of the specific heat and the equivalent increases with the quantity of water, in such a manner, that to an increase of each one equivalent there is a corresponding increase in the product.

15. In the preceding paragraphs I have collated, as far as I know them, the investigations on the specific heat of solid bodies, on the relations of this property to the atomic weight, and on the connexion with the chemical composition of a substance. The views which have been expressed relative to the validity of the law of Dulong and Petit § and that of Neumann, and also as to the question whether the elements enter into chemical compounds with the same specific heats which they have in the free state or with modified ones, are various and often discordant. In this respect it may be difficult to express an opinion which has not been already either stated or hinted at, or which at any rate cannot be naturally deduced from a view previously expressed.

The results to which my investigations on the specific heats of solid bodies have led me are the following:—Each solid substance,

\* Ann Ch. Phys. [3], lvii, 438.

† Berichte der Wiener Akademie der Wissenschaften, xlvi, 248.

‡ Pogg. Ann. cxx, 337 and 579.

§ The universal validity of this law was also defended by Bredow, "On the relation of the Specific Heat to the Chemical Combining Weight." Berlin, 1838. I know this paper only from the mention of it in the new edition of Gehler's "Physicalisches Wörterbuch," vol. x, p. 818. It is also admitted by Mann, in his attempt to deduce this law from the undulatory theory of heat. (1857: Schlomilch and Wiltzschel's "Zeitschrift für Mathematik und Physik," II. Jahrgang, p. 280); and by Stefan, in his investigation on the bearing of this law on the mechanical theory of heat (1859: Berichte der Wiener Akademie, vol. xxxvi, p. 85).



at a sufficient distance from its melting-point, has a specific heat, which may vary somewhat with physical conditions (temperature, greater or less density, amorphous or crystalline conditions, &c.); yet the variations are never so great as must be the case if a variation in the specific heat of a body is to be held as a reason for explaining why the determinations of the specific heats of solid elements do not even approximately obey Dulong and Petit's law, nor those of solid compounds of analogous chemical constitution Neumann's law. Neither law is universally valid, although I have found that Neumann's law applies in the case of many compounds of analogous atomic composition, to which, on account of their totally different chemical department, different formulas are assigned; and even in cases in which these laws have hitherto been considered as essentially true, the divergences from them are material. Each element has the same specific heat in its solid free state and in its solid compounds. From the specific heats to be assigned to the elements, either directly from experimental determination, or indirectly by calculation on the basis of the law just stated, the specific heats of their compounds may be calculated. I show the applicability of this by a great number of examples.

In reference to this calculation of the specific heats of solid bodies I may here make a remark. The agreement between the results of calculation and experiment is often only approximate; and it is important to bring the approximation closer. On the other hand we may be allowed to ask: What means are there of even approximately predicting and calculating before-hand the specific heat of any inorganic or organic solid compound when nothing but its empirical formula is given? to which among the numbers 0.1, 0.2, 0.3 . . . . . may it come nearest? Against *this* uncertainty may be set the differences between calculation and observation, exhibited by the numbers in § 103 to 110.

My proof of the propositions given above is based on determinations made by earlier inquirers, and on a not inconsiderable number of my own. I first describe the method by which I worked, and then give the results which I have obtained by its means.

PART II.—*Description of a method of determining the Specific Heat of Solid Bodies.*

16. I have worked by the method of mixture. It is not neces-

sary to discuss the advantages which this method has over that of the ice-calorimeter, at any rate in requiring smaller quantities; nor, as compared with the method of cooling, need I discuss the uncertainties and differences in the results for the same substance, which are incidental to the use of this method, and which Regnault has detailed.\*

The method of mixtures has been raised by Neumann and by Regnault to a high degree of perfection. Although by Neumann's method it is possible to determine more accurately the temperature to which the body investigated is heated, Regnault's method allows larger quantities to be used and gives the specific heats of such substances as can be investigated by it as accurately as can at all be expected in the determination of this property. In the case of copper and steel, it is not merely possible to determine their specific heats by its means, but also to say whether and how far there is a difference in the first metal according as it has been heated or hammered, and in the second, according as it is soft or hard. It may be compared with a goniometer, which not only measures the angles of a crystal, but also the differences in the angle produced by heat; or it may be compared to a method for determining the specific gravity of a body, by which not only this property, but also its changes with the temperature may be determined. But along with such methods, simpler ones, though perhaps less accurate, have also their value. Which method is the most convenient or which ought to be used in a given case, depends on the question to be decided by the experiment, or on the extent to which the property in question is constant in the substance examined.

With regard to the relations of the specific heat of solid bodies to their atomic weight and to their composition, Regnault's determinations have shown that both Dulong and Petit's and Neumann's laws are only approximate, and that even the accuracy in determining the specific heat which Regnault attempted, and obtained, could not show that these laws were quite accurate.

Although the description of Regnault's mode of experimenting is so widely known, yet it cannot be said to have become the common property of physicists, or to have found an entrance into the laboratories of chemists, to whom the determination of the specific heat is interesting from its relation to the atomic weight.

\* Ann. Ch. Phys. [2] lxxiii, 14; [3] ix, 327.

Very few experiments have been made by this method other than the determinations of Regnault. The method depends on the use of an apparatus which is tolerably complicated and takes up much room. Each experiment requires a long time, and for its performance several persons are required. Regnault has usually worked with very considerable quantities of the solid substance, and in by far the majority of cases at temperatures (usually up to  $100^{\circ}$ ) which many chemical preparations, whose specific heats it is important to know, do not bear. In the sequel I will describe a process, for the performance of which the apparatus can be readily constructed, and for which one operator is sufficient; by which, moreover, the determination of specific heat can be made with small quantities of the solid substance and at a moderate temperature. The method, as I have used it, has by no means the accuracy of that of Regnault; but the results obtained by it are capable of increased accuracy, provided the experiments are executed on a larger scale and within greater ranges of temperature.

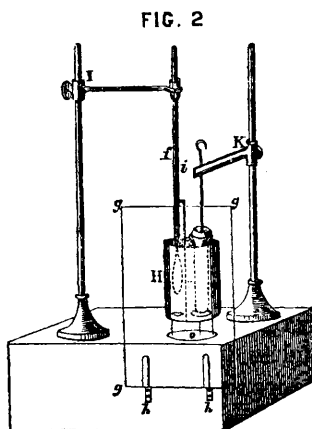
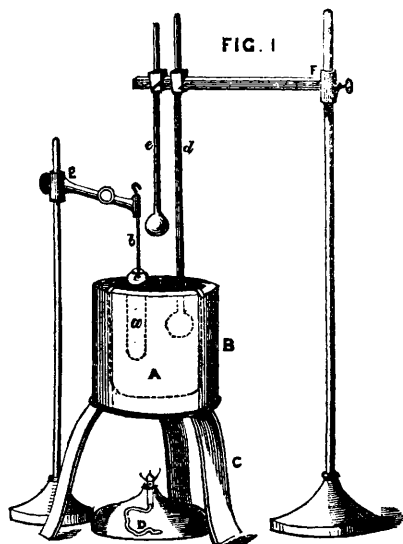
17. The principle which forms the basis of my method is as follows:—To determine the total increase of temperature produced when a glass containing the substance to be investigated, covered by a liquid which does not dissolve it, the whole previously warmed, is immersed in cold water; to subtract from the total increase of temperature that due to the glass and the liquid in it, and to deduce from the difference, which is due to the solid substance, its specific heat.

If, with regard to gain or loss of heat, the glass, in so far as it comes in contact with water, is equivalent to  $x$  parts of water, and if  $f$  is the weight of the liquid in it,  $y$  the specific heat of that liquid,  $m$  the weight of the solid substance,  $M$  the weight of the water in a calorimeter, including the value in water of the immersed part of a thermometer and of the calorimeter,  $T$  the temperature to which the glass and its contents have been heated before immersion in water, and  $T'$  the temperature to which the glass sinks when immersed in the water, while the temperature of the latter rises from  $t$  to  $t'$ , then the specific heat (sp. H.) of the solid substance is

$$\text{sp. H.} = \frac{M(t' - t) - (x + fy) \cdot (T - T')}{m(T - T')}$$

The glass vessel in which the substance is confined ( $a$  in fig. 1) is a tube of glass, the bottom of an ordinary test-tube. In it fits,

but not air-tight, a cork *c*, which is pressed between two small brass plates screwed to a wire *b*. The solid substance to be investigated, in the form of thin cylinders, or in small pieces the size of a pea, along with a liquid of known specific heat, which does not dissolve it, are placed in the tube in such a manner that the liquid covers the solid substance, and that there is a space between the liquid and the cork when it is inserted. The glass, when the cork is fitted, may be suspended to the balance by the wire *b*. Three weighings (1) of the empty glass, (2) after introducing the solid substance, and (3) after introducing the liquid, give the weight of the solid substance (*m*) and of the liquid (*f*).



The heating apparatus (fig. 1) serves to raise the temperature of the glass with its contents. The glass is dipped in a mercury-bath A near its upper edge, and retained by a holder E. The mercury-bath, which consists of a cylindrical glass vessel, is suspended by means of a triangle round the neck of the vessel in an oil-bath B, which stands on a tripod C, and can be heated by a spirit-lamp D. A thermometer *d*,\* fixed to the holder F, is also immersed in the mercury-bath.

The flame of the spirit-lamp may be regulated so that the

\* The figures are one-sixth of the natural size.

thermometer *d* indicates the same temperature for a long time.\* As soon as it may be assumed that the contents of the glass *a* have also risen to this temperature, then, the wire *b* being firmly held in the right-hand by its hook, and the clamp of the holder E in the left, the glass *a* is to be rapidly removed from the heating vessel to the calorimeter H (fig. 2). This is almost the only part of the experiment requiring much practice; the transference of the glass *a* from the one vessel to the other must be effected in an instant, and none of the liquid in the glass must touch the cork.

The calorimeter H stands upon a support G (fig. 2)†, on which there is an oval metal plate *o*. In this there are three depressions, in which fit the three feet of the calorimeter (they are made of very thin hard brass wire). The calorimeter is oval-shaped, and is made of the very thinnest brass plate. In it fits a brass stirrer, made of two parallel plates of equally thin brass, which are joined below by thin wires, and provided with a thin wire ending in a little button *i*, serving as handle. The plates of the stirrer are perforated in such a manner that the glass *a* and a thermometer can be passed through them. Fig. 3 shows more distinctly the construction of the stirrer, also the section of the calorimeter.

For the experiments, the calorimeter is always filled, as nearly as possible, with the same quantity of water. The stirrer is immersed, and a thermometer *f* dipping in the water gives its temperature, which is kept uniform by an upward and downward uniform motion of the stirrer. When the tube *a* is brought into the water of the calorimeter, it is fastened in the clamp of the holder K, which is arranged like the forceps used for blowpipe experiments, so that it stands on the bottom of the calorimeter, and then the stirrer is set to work. This motion of the stirrer, and therewith of the water, must be moderate and uniform in all experiments; this is of some importance for the uniformity and comparability of the experiments. The temperature indicated by

\* In order to obtain temperatures constant at about 50°, a spirit-lamp with a thin wick is used, and this is pressed in the sheath so that the alcohol-vapour above it burns with a very small flame. The position of the wick and the intensity of the flame may be conveniently regulated if the upper part of the wick is surrounded by a spiral of thin copper wire whose ends project from the sheath.

† In making the experiment, the actual distance between the calorimeter and the heating apparatus must be greater than is indicated in the figure, but not so great that the glass *a* cannot, by a rapid motion of the arm, be transferred from the mercury-bath to the calorimeter.

the thermometer  $f$  rises and soon attains its maximum, which continues for some time, and can be observed with certainty. With this the experiment is concluded. The tube  $a$  can be taken from the calorimeter, dried, and used for a new experiment.

The increase of temperature produced in the calorimeter by the tube  $a$  and its contents, would be incorrectly given if the warmth of the body of the operator, who moves the stirrer and observes the thermometer, acted on the calorimeter. This is prevented by a glass screen  $g g g$ , fig. 2, which is fitted in the brackets  $h h$ , and above which the handle of the stirrer projects.

18. This process for determining the specific heat of solid bodies has the following advantages over those hitherto principally used:—The use of the mercury-bath makes it possible readily to produce, and maintain for any adequate length of time, any temperature desirable in such experiments. The mercury-bath\* shares with the air-bath the advantage that nothing which might influence the thermal effect in the calorimeter can adhere to the substance heated in it (in this case the tube and contents) when it is removed. Over the air-bath it has the advantage that any body placed in it takes the temperature of the surrounding medium much more quickly through its entire mass. The communication of heat to the solid substance is materially promoted by the circulation of the liquid in the tube between its particles the time necessary for the entire contents of the glass to become equally heated is a very short one. Moreover, this very circulation of the liquid between the particles of the solid ensures a quicker and more uniform transmission of the heat of the contents of the glass to the water of the calorimeter; the maximum temperature of this water is soon attained, although the transmission of the excess of temperature must take place through the sides of the glass.

The apparatus just described is very simple. It is readily constructed; the chief point is to have two thermometers which have been compared with each other, one of them ( $f$ ) graduated in tenths of a degree, while on the other ( $d$ ) the tenth of a degree can be observed with certainty. The apparatus does not require much space; yet, while the experiment is being made, rapid changes in the temperature of the surrounding air must be avoided.

\* In 1848 I already used such a one for heating liquids enclosed in glass tubes, in determining their specific heats (Poggendorff's "Annalen," vol. lxxv, p. 98).

One observer only is required. The experiments which I shall communicate prove that, by means of this apparatus, the specific heat of solid substances, even when only small quantities are taken (in most cases I worked with only a few grammes), may be determined with an accuracy not much less than that attained with larger quantities in more complicated processes.

20. In order to appreciate the trustworthiness of the results arrived at by my mode of experiment, it is important to state with what amount of accuracy the data of observation and the ancillary magnitudes were determined.

For observing the temperature of the water in the calorimeter, I used thermometers made by Geissler, of Bonn, which the kindness of Professor Buff, Director of the Physical Cabinet in Giessen, placed at my disposal. In these thermometers the tube consists of a fine glass thread drawn out at the lamp. The bulb is cylindrical, very thin in the glass, and contains but little mercury. On one (*b*)  $1^{\circ}$  C. corresponds to a length of almost 5 millims. on the scale, and on the other (*r*) to almost 4.5 millims. Tenths of a degree can be read off directly on the scale, and it is easy to learn to estimate hundredths safely. I have repeatedly compared these two thermometers, between  $7^{\circ}$  and  $24^{\circ}$ , with two normal thermometers of my own construction, which agree very well with each other, and on one of which a division corresponds to  $0^{\circ}.4878$ , and the other to  $0^{\circ}.4341$ . The differences of the indications between the Geissler's thermometers and these could be considered as constant with those limits; for the differences thus observed all the readings made with the Geissler's thermometers had to be corrected to make them comparable with the indications of the normal thermometer.

The temperature of the mercury-bath was ascertained by means of one of these normal thermometers, and the indications of this thermometer immersed in the bath (*d* in fig. 1.) corrected for the lower temperature of the mercury-thread out of the bath; this latter temperature was given with adequate approximation by the second thermometer, *e*.\*

21. The weight of the thin sheet-brass calorimeter, together with stirrer, was 11.145 grms.† Taking the specific heat of brass,

\* The paragraphs in this abstract are numbered as in the original memoir.

† At the beginning of these investigations. During their progress the calorimeter was cleaned and dried with bibulous paper a countless number of times, so that its weight diminished by about  $0.04$  grm. in the course of the experiments. In deter-



according to Regnault, at 0.09391, the calorimetric value in water of this mass of metal is 1.046 gm. Considering that the calorimeter in the experiments was not quite filled with water, but about  $\frac{1}{4}$ th remained empty, even after introducing the tube, I put the value in water at 0.872.

In determining the calorimetric water value of the immersed parts of the thermometers,  $r$  and  $b$ , the following experiments were made. The weight of water in the calorimeter, together with the reduced weight of the metal, was 30.87 grms. When the thermometer  $r$  heated to  $33^{\circ}.86$  was immersed, the temperature rose from  $10^{\circ}.73$  to  $10^{\circ}.85$ ; the immersion of the thermometer  $b$  at a temperature of  $37^{\circ}.53$  caused a rise from  $10^{\circ}.61$  to  $10^{\circ}.76$ . In both cases the temperature of the water was indicated by means of the other thermometer, the reduced value of which might be neglected under these circumstances. These experiments gave 0.16 as the reduced value of the thermometer  $r$ , and 0.17 as the reduced value of the thermometer  $b$ . The thermometers have very nearly the same dimensions. Hence I put the reduced value of the calorimeter (that is, of the part of the metal concerned), of the stirrer, and of the immersed part of the thermometer a 1.04 gm. Even if this determination is a few tenths out, it is scarcely appreciable as compared with the quantity of water in the calorimeter. In all following experiments this was between 25.85 and 25.95 grms.

All the subsequent determinations depend on fixing differences of weights and of temperatures. The accuracy of the results depends on the precision with which both kinds of magnitudes are ascertained; and it is useless to determine the weights to  $\frac{1}{1000}$  or nearer, if the differences in temperature cannot be determined more accurately than to  $\frac{1}{200}$  or  $\frac{1}{300}$ . I have weighed to centigrammes instead of to milligrammes, by which the time necessary for the weighings is much shortened, and their accuracy not materially lessened.

22. The reduced value  $x$  remained to be determined of the glasses (cylindrical tubes of thin glass, see § 17), or, rather, of that part which was immersed in the water of the calorimeter, the quantity of which was always the same. In the following,  $T$  is the temperature to which the glass in the mercury-bath was heated (compare fig. 1),  $M$  the quantity of water in the calorimeter, the weight of water used in each experiment, the weight which the calorimeter actually had at the time was taken as basis.

meter + the reduced value in water of the other parts of the latter, which required to be taken into account,  $t$  the temperature of the water in the calorimeter when the glass was immersed (fig. 2), and  $\tau$  the temperature to which the water became heated, and which must be considered as that to which the glass cooled.\* We have then

$$x = \frac{M(\tau - t)}{T - \tau}.$$

In my experiments I used three glasses, which may be called 1, 2, and 3. To ascertain the reduced value of glass 1, I made the following determinations :—

Temperature of Air 15°·8.

T.	$\tau$ .	$t$ .	M. grms.	$x$ .
78·54	17·23	15·72	26·98	0·664
74·38	17·16	15·78	26·97	0·651
75·51	17·14	15·72	26·92	0·655
76·06	17·15	15·73	26·945	0·649
77·32	17·22	15·74	26·96	0·664
			Mean..	0·657

A second series of experiments, made in a similar manner, to determine the reduced value for glass 1 gave the following results :—

Temperature of the Air 19°·9–19°·8.

T.	$\tau$ .	$t$ .	M. grms.	$x$ .
78·50	21·32	19·93	26·99	0·656
81·86	21·47	20·03	26·98	0·643
80·42	21·43	20·02	26·98	0·645
79·77	21·42	20·03	26·935	0·642
80·14	21·51	20·12	26·955	0·639
			Mean..	0·645

The mean of these two means, 0·657 and 0·645, gives as the reduced value in water of glass 1, 0·651 grm.

\* If the cork which closes the glass, and by means of the wire passing through it enables it to be handled, is moist, incorrect and discordant values are obtained for it, owing to the evaporation of water in the empty glass so long as this is in the mercury-bath, and to the condensation of aqueous vapour in the glass when it is immersed in the calorimeter.

In like manner, the reduced water-value of glass 2, was found to be 0.487, and that of glass 3 was found to be 0.453.

23. In those experiments in which a glass containing a liquid and perhaps a solid substance is immersed, while warm, in the water of the calorimeter, it may be asked if, when the water has become heated to a certain maximum temperature, the contents of the glass have actually cooled to the same temperature. In earlier experiments made by the method of mixture, it was at once assumed that the temperature assumed by the water of the calorimeter after immersing the solid was actually that also to which the immersed body sank. Neumann has taken into account that the immersed body, when the water shows its maximum temperature, may have a somewhat higher temperature.\* Avogadro has also taken this into account,† and Regnault has also allowed for this circumstance in the case in which the mass, immersed in the water of the calorimeter, is a bad conductor of heat.‡ A correction for this fact is certainly inconsiderable and unnecessary if the immersed body conducts heat well, and the range of temperature through which it cools in the liquid is great. This interval of temperature was in my experiments considerably smaller than in those of Neumann and of Regnault; and as in my experiments the excess of heat of the contents of the glass had to pass through its sides to the water of the calorimeter, it might be doubted whether, when the temperature of the water was at its maximum, this temperature could be considered as that of the contents of the glass.

I have endeavoured to answer these questions experimentally. A glass, such as was used for holding the solid investigated and a liquid, was filled with water, and a perforated cork fitted, by means of which the glass could be handled. The glass filled with water was warmed, and then placed in the calorimeter filled with water; a thermometer A, passing through the cork, showed the temperature of the water in the glass; a second, B, showed that of the calorimeter-water. If the glass filled with the warmer water is immersed in the cold water, the following circumstances are observed.§ A sinks very rapidly, while B rises more slowly;

\* In the memoirs mentioned in § 4, Pape has also discussed and applied the correction to be made for the above circumstance (Pogg. Ann. cxx, 341).

† Ann. Ch. Phys. [2] lv, 90.

‡ Ibid [2] lxxiii, 26.

§ In these experiments, in order to insure uniformity in the temperature of the water, the stirrer was kept in continual motion, and the same process followed as in ascertaining the specific heat.

if B shows the maximum temperature for the water of the calorimeter (this temperature being called  $t'$ ), A gives a higher temperature ( $T$ ) for the contents of the glass. B then slowly sinks and A follows it, while the difference between  $t'$  and  $T$  always becomes smaller. In the two following series of experiments, I have endeavoured to determine by how much, under certain conditions, the temperature  $T'$  of the water in the glass exceeds the maximum temperature  $t'$  of the water in the calorimeter when this maximum temperature as such is observed. I obtained the following results: the temperature of the air in the experiments was  $13^{\circ}2-13^{\circ}5$ .

Experiments with Glass 1.			Experiments with Glass 2.		
$T'$ .	$t'$ .	Difference.	$T'$ .	$t'$ .	Difference.
15·51	15·13	0·38	15·71	15·50	0·21
14·96	14·72	0·24	15·96	15·65	0·31
16·11	15·94	0·17	15·16	14·91	0·25
15·56	15·36	0·20	14·76	14·47	0·29
14·24	14·05	0·19	14·66	14·33	0·33
15·96	15·64	0·32	15·56	15·24	0·32

A closer agreement in the numbers expressing the difference between  $T'$  and  $t'$  is difficult to attain, since a certain time is necessary to observe the occurrence of the maximum temperature, and during the time in which the thermometer B remains constant, the thermometer A still sinks; according to the moment at which the maximum temperature is considered to be established, this difference may be obtained different, and the smaller the later the observation is made. Moreover the magnitude of this difference between  $T'$  and  $t'$  depends on the difference between  $t'$  and the temperature of the air. I have always endeavoured to work under the same circumstances, and especially to arrange the experiments so that the maximum temperature of the water in the calorimeter did not exceed by more than  $2^{\circ}$  the temperature of the air\*. For these experiments and the apparatus which I

\* A preliminary experiment shows how cool the water in the calorimeter ought to be. Water which is somewhat cooler than the surrounding air may be kept in stock for such experiments by placing it in a cylindrical flask covered externally with filtering paper, and standing in a dish of water, so that the paper is always moist. To warm the water in the calorimeter, it was merely necessary, with apparatus of the the dimensions I used, to lay the hand on it for a short time.

used, I assumed, on the basis of the preceding experiments, that if the water of the calorimeter had assumed its maximum temperature  $t'$ , the contents of the glass were  $0^{\circ}\cdot 3$  higher; that is, I put throughout  $T'$ , the temperature to which the contents of the glass immersed in the calorimeter had fallen,  $=t' + 0^{\circ}\cdot 3$ .

24. It is a matter of course that, in introducing this correction for obtaining the temperature of the contents of the glass at the time the maximum temperature has been attained in the calorimeter, it is unnecessary to give the indications of  $T'$  in hundredths of a degree; and since the temperature  $T$ , to which the glass with its contents was heated in the mercury-bath, only serves to deduce the difference  $T - T'$ , it is unimportant in giving this temperature to do so in hundredths of a degree. The accuracy of the determinations of specific heat, in so far as it depends on determinations of temperature, is limited by the accuracy with which the difference  $T - T'$  and  $t' - t$  are determined (where  $t$  is the original temperature of the water in the calorimeter, and the other letters have the meanings previously assigned to them). To have one of these differences very accurately, while the other is much less accurately determined, avails nothing for the accuracy of the final results. It is at once seen that in my experiments, and especially in those of Neumann and Regnault, the hundredths of a degree have a greater significance for the small difference  $t' - t$ , than the tenths of a degree for the great difference  $T - T'$ .

The correction for educing the value of  $T'$ , which I have just discussed, is of course more important the smaller the difference  $T - T'$ ; for most of my experiments in which this difference is about  $30^{\circ}$ , the significance of this correction is inconsiderable, if the contents of the glass be a good conductor. I give a few numbers. The experiments given in § 25 on the specific heat of mercury, which, by using this correction, give it at  $0\cdot 0335$  in the mean, give it  $=0\cdot 0331$  if this correction is neglected, that is  $T'$  made  $=t'$ . The fourth series of experiments, given in § 27, for determining the specific heat of coal-tar naphtha A, give it at  $0\cdot 425$  when this correction is made, and at  $0\cdot 420$  when it is omitted. The first series of experiments in § 33, for determining the specific heat of sulphur, give it at  $0\cdot 159$  when this correction is used, and at  $0\cdot 152$  when it is neglected. Whether in all such cases  $T'$  is put  $=t'$ , or  $=t' + 0^{\circ}\cdot 3$ , is of considerable importance. The correction in question is inadequate if the substance in the

glass is a bad conductor ; for example, when the solid in the glass is a pulverulent or porous mass, in which the moistening liquid stagnates (compare § 18). That, under such circumstances, the numbers obtained for the specific heat are found somewhat too small must be remembered in the case of chromium, and in that of chloride of chromium. Too small numbers are also obtained, if in the experiments the maximum temperature of the cooling water exceeds that of the air by much more than 2°. Such experiments are not comparable with the others, for example, with those made for the purpose of ascertaining the ancillary magnitudes occurring in the calculation of the results ; for them this correction is inadequate, and the loss of heat which the contents of the calorimeter experiences between the time which elapsed between immersing the glass and the establishment of the maximum temperature, is too great.

25. I first attempted to test my method by some experiments in which water or mercury was placed in the calorimeter. For the specific heats of these liquids the following numbers were obtained, calculated by the formula :—

$$\text{sp. H} = \frac{M(t' - t) - x(T - T')}{f(T - T')}$$

in which the signification of  $f$  is manifest from what follows, that of the other letters from what has been given before.

In the experiments in which a readily vaporizable liquid was contained in the glass, such as water, or coal-tar naphtha, a sensible formation of vapour took place, although the temperature did not exceed 50°. If the glass containing the liquid was heated in the mercury-bath, vapour was formed in the empty space below the cork which served as stopper ; if the glass was then brought into the water of the calorimeter, this vapour condensed and settled partially on the stopper. The stopper did not act materially on the water of the calorimeter. The quantity of liquid in the glass which acted directly on the water of the calorimeter, decreased somewhat in each experiment ; but this decrease is very inconsiderable. In the following experiments,  $f$  denotes first the weight of the liquid in the glass at the commencement of the experiment, and at last its weight at the end of the experiments, that is, after subtracting the liquid which had vaporized and condensed on the stopper. After the end of the experiment the stopper was dried to remove the liquid, and by another weighing

of the glass, together with its contents and stopper, the weight of the liquid still contained in the glass was obtained. The decrease of weight of the liquid in the glass was always found to be considerable, and might without any harm have been neglected; for the last experiment of a series I have always taken the diminished weight of the liquid into account, but for those between the first and the last I have neglected the diminution of the weight of the liquid in the glass. In the following tables, the values of  $f$  marked with an asterisk, are those which were formed after drying the stopper.

Two series of experiments in which *water* was contained in the glass, gave the following results for the specific heat of this liquid:—

Experiments with Glass 1. Temperature of the Air 19°·0.

T.	T'.	t.	t.	M.	f.	z.	sp. H.
°	°	°	°	grms.	grms.	grm.	
45·2	20·9	20·62	16·83	26·945	3·43	0·651	1·035
46·6	21·2	20·92	17·03	26·935	"	"	1·013
47·4	21·3	20·96	17·03	26·965	3·42*	"	0·917

Experiments with Glass 3. Temperature of the Air 19°·0.

T.	T'.	t.	t.	M.	f.	z.	sp. H.
°	°	°	°	grms.	grms.	grm.	
46·8	21·1	20·76	17·03	26·95	3·445	0·453	1·004
46·8	21·1	20·83	17·12	26·985	"	"	0·999
47·0	21·2	20·93	17·22	26·935	3·435*	"	0·996

The value found for the specific heat of the contents of the glass comes very near the number 1, assumed for the specific heat of water.

Determinations in which *mercury* was contained in the glass gave the following results for the specific heat of the contents of the glass.

Experiments with Glass 1. Temperature of the Air 13°·8–14°·4.

T.	T'.	t.	t.	M.	f.	z.	sp. H.
°	°	°	°	grms.	grms.	grm.	
51·1	16·8	16·50	13·41	26·945	53·015	0·651	0·0335
48·5	16·8	16·48	13·64	26·95	"	"	0·0333
45·2	16·5	16·20	13·63	26·965	"	"	0·0333

Experiments with Glass 2. Temperature of the Air 13°·8–14°·4.

T.	T'.	t.	t.	M.	f.	z.	sp. H.
°	°	°	°	grms.	grms.	grm.	
50·0	17·1	16·79	13·74	26·935	60·015	0·437	0·0335
45·6	16·7	16·41	13·72	26·935	"	"	0·0337



The mean of these five determinations gives 0.0335 for the specific heat of mercury, in accordance with the results found by other observers for this metal (0.0330 between 0° and 100°, Dulong and Petit; 0.0333, Regnault).

26. For the liquid which is to be placed in the glass along with the substance whose specific heat is to be investigated, I could in many cases use water; but many substances, the determination of which is important, dissolve in water, and hence I had to use a different liquid. Coal-tar naphtha has the advantage that it is a mobile liquid, does not dissolve most salts, and does not resinify in contact with the air; but its odour is very disagreeable especially on continuous working, respiring air charged with its vapour appears to act injuriously on the organs of the voice. As compared with water, coal-tar naphtha has the disadvantage, that its specific heat must be specially determined, and any possible uncertainty in this is transferred to the determination of the specific heat of the solid substance; but the thermal action of a given volume of naphtha is only about  $\frac{1}{3}$  that of the same volume of water; and in experiments in which the thermal action of a solid substance is determined, along with that of the necessary quantity of liquid which is contained with that substance in a glass, the thermal action due to the solid is a larger fraction of the total if coal-tar naphtha is used than if water is the liquid, which is a favourable circumstance in the accurate determination of specific heat. As it was more especially important to obtain comparability in the results for specific heat, I have, for a great many substances which are insoluble in water, and for whose investigation water might have been used, also employed coal-tar naphtha. Water was used for a few substances which are soluble in coal-tar naphtha (sulphur, phosphorus, sesquichloride of carbon, for instance). Several substances I determined both with water and with naphtha; the results thus obtained agree satisfactorily. To the question as to whether any possible change in the specific heat of naphtha with the temperature can be urged against the use of this liquid, I shall return in a future paragraph.

27. The coal-tar naphtha A which I principally used in the subsequent experiments was prepared from the commercial mixture of hydrocarbons  $C_nH_{2n-6}$ , by purifying it with sulphuric acid, treating the portion which distilled between 105° and 120° with chloride of calcium for six days, then again rectifying it, and collecting separately that which passed between 105° and 120°.

This liquid had the specific gravity 0·869 at 15°. Four series of experiments, made to determine its specific heat, gives as a mean result, the number 0·431, between 14° and 52°.

Another sample of coal-tar naphtha, B, used in some of the experiments was found to have a specific heat = 0·419 between 20° and 50°.

29. My experiments were made at very different temperatures. The temperature of the air was often something under 10°, sometimes above 20°. These numbers represent the limits to which the liquid in the glass, together with the solid substance, cooled in the calorimeter. In most experiments I heated the glass with its contents to about 50°, in some cases not so high. Now, for the various intervals of temperature within which the liquid in the glass cooled, can its specific heat be assumed to be always the same? For water this may be done, and for coal-tar naphtha I did not doubt it while engaged in my experiments. I first, when they were finished, became acquainted with Regnault's\* investigations on the specific heat of liquids at various temperatures; according to these experiments the specific heat of some liquids considerably increases with the temperature. I have not directly investigated coal-tar naphtha in this respect, but it is probable that the specific heat of this mixture of hydrocarbons  $C_n H_{2n-6}$ , alters but little with the temperature, and it is certain that this change is without influence on the accuracy of my determinations of the specific heats of solid substances. Regnault's experiments†, made by the method of cooling, show no change for benzole,  $C_6H_6$ , between 20° and 5°, while there is a distinct change in the case of alcohol. For pure benzole‡ I found the specific heat by the method of mixture to be 0·450 between 46° and 19°; Regnault§ found it between 71° and 21° to be 0·436. These numbers, obtained with different preparations, are not indeed comparable for a decision of the question just discussed, but they render improbable a considerable increase in the specific heat of benzole with the temperature. What I more especially lay weight upon is this: the specific heats of solids which I have determined at various temperatures, by their agreement with the

\* Relation des expériences . . . pour déterminer les lois et les données physiques nécessaires au calcul des machines à feu, vol. ii, p. 262 (1862).

† Ann. Ch. Phys. [3] ix, 336 and 349.

‡ Pogg. Ann. lxxv, 107.

§ Relation, &c. . . . , ii, 283.

numbers previously found by others, do not indicate any influence of a change of specific heat of naphtha with the temperature.

In the preceding method of experiment, whether water or naphtha of the kind described is contained in the vessel, a temperature much higher than  $50^{\circ}$  cannot be employed; for otherwise the quantity of liquid evaporating and condensing on the stopper becomes far too considerable. Perhaps with hydrocarbons of higher boiling-points higher temperatures might be ventured upon.

PART III.—*Determination of the Specific Heat of Individual Solid Substances.*

31. By the method whose principle and mode of execution have been discussed in the preceding paragraphs I have determined, the specific heat of a large number of solid substances.\* I should have liked to include a still larger number of bodies in my investigations; but a limit was put by the straining of the eyes from constant reading of finely divided scales, and by the injurious action which the long-continued working with coal-tar naphtha produces.

32. The signification of the letters in the statement of the following experiments and their calculation is clear from § 17; in reference to the value of the numbers for M, compare § 21, for  $x$  § 22, for T' § 23;  $y$  denotes the specific heat of the water or naphtha used in the experiments.

33. *Sulphur*: pieces of transparent (rhombic) crystals from Girgenti. I made three series of experiments with this substance.

I.—Experiments with Water. Glass 1. Temperature of the Air  $13^{\circ}2$ .

T.	T'.	$t$ .	$t$ .	M.	$m$ .	$f$ .	$y$ .	$z$ .	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
45.8	15.5	15.24	11.74	26.95	4.16	1.765	1.000	0.651	0.168
46.0	16.2	15.93	12.52	26.935	"	"	"	"	0.160
45.2	16.0	15.73	12.42	26.945	"	"	"	"	0.153
45.8	16.4	16.05	12.74	26.96	"	1.75	"	"	0.153
Mean ..									0.159

\* We give in this abstract only a few of Professor Kopp's determinations in detail, referring for the rest to the original paper.—ED.

## II.—Experiments with Water. Glass 2. Temperature of the Air 13°·2.

T.	T′.	t′.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
45·8	16·4	16·07	12·36	26·96	4·815	2·09	1·000	0·487	0·171
47·3	16·6	16·33	12·46	26·95	„	„	„	„	0·170
44·1	16·5	16·15	12·74	26·925	„	„	„	„	0·156
45·1	16·6	16·28	12·77	26·96	„	2·07*	„	„	0·159
Mean ..									0·164

## III.—Experiments with Water. Glass 3. Temperature of the Air 17°·2.

T.	T′.	t′.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
43·7	19·1	18·83	15·79	26·99	4·92	2·065	1·000	0·453	0·166
43·5	19·1	18·84	15·84	26·97	„	„	„	„	0·162
43·3	19·2	18·92	15·92	26·94	„	„	„	„	0·170
43·1	19·2	18·87	15·93	27·98	„	2·05*	„	„	0·166
Mean ..									0·166

Taking the mean of the means obtained in the three series of experiments, 0·159, 0·164, 0·166, we obtain 0·163 as the specific heat of rhombic sulphur between 17° and 45°. By the method of cooling, Dulong and Petit found the specific heat of sulphur at the mean temperature to be 0·188; Neumann found 0·209 by the method of mixture; for sulphur which had been purified by distillation, fused and cast in rolls, Regnault found† the specific heat between 14° and 98° to be 0·2026. In these experiments a development of heat depending on a change from amorphous sulphur into rhombic-crystallised appears to have co-operated, and to have caused the circumstance observed by Regnault, that after immersing the heated sulphur in the water of the calorimeter, the maximum temperature was set up only after an unusually long time. Sulphur which has solidified after being melted, usually contains an admixture of amorphous sulphur—the greater the more the melting point has been exceeded—which, at the ordinary temperature passes slowly, at 100° more rapidly, into crystallised, accompanied by disengagement of heat. The transformation of the sulphur set up by the heating, and continued in the water of the calorimeter, brought about this slow appearance of the maximum temperature, and made the specific heat appear too great;

\* After drying the stopper.

† Ann. Ch. Phys. [2] lxxiii, 50.

for Regnault's subsequent determinations,\* also made between 97° and 99° and the mean temperature, gave it considerably less; 0.1844 for freshly melted sulphur (in which superfusion had been avoided?); 0.1803 for sulphur which had been melted two months; 0.1764 for what had been melted two years (and which had then given 0.2026); 0.1796 for sulphur of natural occurrence. The difference between the latter result and my own doubtless depends, partially at least, on the fact that Regnault's determination was made between 14° and 99° (the latter of which temperatures is very near the melting point of rhombic sulphur); mine was made between 17° and 45°.†

34. *Boron*.—I have made some experiments with this substance, which have some interest for the question whether this body has essentially different specific heats in its different modifications; but the results are not very trustworthy, owing to the spongy nature of the amorphous boron and the doubtful purity of the crystallised variety.

The *amorphous Boron*‡ which I investigated was pressed in small bars, and had stood several days *in vacuo* over sulphuric acid.

Experiments with Naphtha A. Glass 1. § Temperature of the Air 17°·0—17°·2.

T.	T'.	t.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grm.	grms.		grm.	
49·0	18·7	18·73	16·36	26·955	1·52	2·515	0·431	0·651	0·246
48·1	18·6	18·55	16·23	26·965	"	"	"	"	0·254
48·0	18·6	18·64	16·33	26·95	"	"	"	"	0·252
47·9	18·7	18·72	16·42	26·95	"	2·49	"	"	0·262
Mean ..									0·254

Even if the results of the individual experiments agree tolerably with each other they are not very trustworthy; for the quantity of boron (only 1½ grm.) is very small, and the amount of heat due to the boron is a very small part of the total (comp. § 19). Yet I do not consider the result of the above series of experiments (that

\* Ann. Ch. Phys. [3] ix, 326 and 344.

† There is nothing known certainly as to whether the different modifications of sulphur have essentially different specific heats. Marchand and Scheerer's experiments on brown and yellow sulphur made by the method of cooling, compare in *Journal für Prakt. Chemie*, vol. xxiv, p. 153.

‡ "Prepared from boracic acid by sodium, and treated with hydrochloric acid."—Wöhler.

§ See page 177.

|| After drying the stopper.

between  $18^{\circ}$  and  $48^{\circ}$  the specific heat of amorphous boron is about 0.254) as very far from the truth. There are no considerable accidental errors of observation in these experiments, to judge from their agreement with one another. Of the constants for calculating the experiments,  $x$  and  $y$  must be taken into account in regard to any possible uncertainty. It has been assumed that  $x=0.615$  and  $y=0.431$ ; if we took  $x=0.63$  and  $y=0.41$ , the specific heat as the mean of four experiments would be  $=0.30$ ; if  $x$  were  $0.67$  and  $y=0.45$ , the specific heat would be  $0.21$ . But from what has been communicated in § 22 and § 27 in reference to the determination of  $x$  and  $y$ , it cannot be assumed that any possible uncertainty in reference to these values can reach either of the above limits. It can be assumed with the greater certainty that the specific heat of amorphous boron is between  $0.2$  and  $0.3$  and nearly  $0.25$ , because  $x$  and  $y$  could not simultaneously both be found too great or too small (if  $x$  had been too small  $y$  would have been too great, and *vice versa*).

*Crystallised Boron\*.*

Experiments with Naphtha A. Glass 3. Temperature of the Air  
 $18^{\circ}.9-18^{\circ}.7$ .

T.	Tv.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
50.9	20.8	20.52	18.53	26.94	2.82	1.53	0.431	0.453	0.237
51.3	20.8	20.52	18.52	26.975	"	"	"	"	0.233
51.5	20.8	20.53	18.53	26.985	"	"	"	"	0.229
51.4	20.8	20.46	18.43	26.99	"	1.52†	"	"	0.222
Mean ..									0.230

Hence the specific heat of the crystallised (adamantine) boron investigated is  $0.230$  between  $21^{\circ}$  and  $51^{\circ}$ ; it is pretty near that found for amorphous boron,  $0.254$ . Regnault found ‡ (between  $98^{\circ}$  and  $100^{\circ}$  and the mean temperature)  $0.225$  for a specimen of crystallised boron prepared by Rousseau;  $0.257$  for one prepared by Debray;  $0.262$  for one obtained from Deville; and  $0.235$  for a specimen of graphitic boron prepared by Debray. The specific heat of amorphous boron could not be determined by

\* " Made in Paris, probably by Rousseau, and doubtless by melting borax with aluminium. To conclude from its external appearance, it probably contained some aluminium and carbon; compare the analysis in Ann. Ch. Pharm. ci. 347.

† After drying the stopper.

‡ Ann. Ch. Phys. [3] lxxiii, 31.

Regnault's method, because, when heated to  $100^{\circ}$  in air, it partially oxidizes into boracic acid, with disengagement of heat (three experiments, in which the quantity of boracic acid formed was determined, and its specific heat, but not the thermal action due to the formation of hydrated boracic acid in immersion in water allowed for, gave respectively 0.405, 0.348, and 0.360, which numbers Regnault does not consider as even approximately representing the specific heat of amorphous boron), and when greatly cooled disengages a quantity of air when immersed in warmer water, which renders the results uncertain.

36. *Carbon*.—It is known how different are the numbers obtained for the specific heat of carbon in its different forms. I have determined the specific heat for comparatively only a few of the modifications of carbon—for gas-carbon, for natural and artificial graphite. Before the experiment, each of these substances was strongly heated for some time in a covered porcelain crucible, and then allowed to cool, and immediately transferred to the glass for its reception, and, after weighing, naphtha was poured over it.

*Gas-carbon* from a Paris gas-works; very dense, of an iron-grey colour; left very little ash when calcined.\* It was used in pieces the size of a pea, and two series of experiments were made.

I.—Experiments with Naphtha A. Glass 1. Temperature of the Air  $18^{\circ}9$ — $19^{\circ}2$ .

T.	T'.	t'.	t.	M.	m.	f.	y.	z.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
52.9	20.8	20.53	18.13	26.955	3.135	1.825	0.431	0.651	0.184
52.6	20.9	20.63	18.26	26.98	"	"	"	"	0.185
51.7	20.7	20.42	18.06	26.97	"	"	"	"	0.196
52.4	20.9	20.58	18.23	26.98	"	1.805†	"	"	0.186
Mean ..									0.188

\* This carbon, as well as the above-mentioned varieties of graphite, was analyzed in the Laboratory at Giessen by Mr. Huber. The gas-carbon gave, when placed in a platinum boat and burned in a stream of oxygen—

	I.	II.	III.	IV.	V.
Carbon .....	97.19	98.25	97.73	98.08	98.55
Hydrogen .....	0.53	0.15	0.68	9.37	1.00
Ash .....	0.61	0.62	0.73	0.23	0.69
	98.33	99.02	99.14	98.68	100.24

† After drying the stopper.



## II.—Experiments with Naphtha A. Glass 3. Temperature of the Air 20°·5—20°·8.

T.	T'.	t'.	t.	M.	m.	f.	y.	z.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
52·6	22·6	22·33	20·23	26·985	3·345	1·935	0·431	0·453	0·180
52·2	22·5	22·23	20·14	26·985	"	"	"	"	0·183
52·3	22·5	22·20	20·12	26·965	"	"	"	"	0·179
52·5	22·6	22·31	20·22	26·955	"	1·91*	"	"	0·182
Mean ..									0·181

These determinations give, as the average of means of both sets of experiments, the number 0·185 as the specific heat of gas-carbon between 22° and 52°.

*Natural graphite* from Ceylon. Left very small quantities of ash when calcined.†

## I.—Experiments with Naphtha A. Glass 3. Temperature of the Air 18°·9—19°·2.

T.	T'.	t'.	t.	M.	m.	f.	y.	z.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
51·4	20·8	20·48	18·13	26·975	4·025.	2·085	0·431	0·453	0·179
51·4	20·8	20·51	18·13	26·99	"	"	"	"	0·186
51·8	20·8	20·54	18·15	26·975	"	"	"	"	0·181
52·0	20·8	20·54	18·13	26·99	"	2·06*	"	"	0·183
Mean ..									0·183

## II.—Experiments with Naphtha A. Glass 1. Temperature of the Air 19°·0—18°·7.

T.	T'.	t'.	t.	M.	m.	f.	y.	z.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
53·9	21·1	20·77	18·22	26·97	3·515	1·935	0·431	0·651	0·174
52·2	21·0	20·73	18·31	26·96	"	"	"	"	0·176
52·1	21·2	20·86	18·52	26·94	"	"	"	"	0·158
53·0	21·0	20·73	18·32	26·97	"	"	"	"	0·155
52·8	21·0	20·73	18·33	26·965	"	1·91*	"	"	0·160
Mean ..									0·165

\* After drying the stopper.

† In Mr. Huber's analyses this substance was placed in a platinum boat, then burned in a porcelain tube in oxygen.

	I.	II.	III.
Carbon .....	..	99·11	98·52
Hydrogen .....	..	0·17	0·06
Ash .....	0·26	0·27	0·51
		99·55	99·09

The residual porous ash left after the combustion was tolerably white, with admixed red particles.

III.—Experiments with Naphtha A. Glass 3. Temperature of the Air 19°·9—20°·0.

T.	T'.	t.	t.	M.	m.	f.	y.	z.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
51·6	21·9	21·55	19·33	26·97	3·90	2·05	0·431	0·453	0·174
51·3	22·0	21·71	19·52	26·955	„	„	„	„	0·174
51·5	22·0	21·70	19·52	26·97	„	„	„	„	0·168
51·5	21·9	21·63	19·42	26·96	„	2·04*	„	„	0·175
Mean ..									0·173

The average of the means of these three series of determinations, 0·183, 0·165, and 0·173, gives 0·174 as the specific heat of Ceylon graphite between 21° and 52°.

*Iron graphite* from Oberhammer, near Sayn, separated upon black ordnance iron. Thin, very lustrous laminae, freed from iron by treatment with aqua regia as much as possible, yet not completely.†

I.—Experiments with Naphtha A. Glass 3. Temperature of the Air 19°·0—18°·7.

°	T'.	t.	t.	M.	m.	f.	y.	z.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
52·5	20·8	20·53	18·21	26·955	2·51	2·445	0·431	0·453	0·186
52·9	21·1	20·84	18·54	26·98	„	2·565‡	„	„	0·156
51·4	20·9	20·64	18·43	26·94	„	„	„	„	0·157
52·0	20·9	20·60	18·33	26·99	„	2·545*	„	„	0·168
Mean ..									0·167

\* After drying the stopper.

† This iron graphite, according to Mr. Huber's analyses, in which it was also burned in oxygen in a platinum boat placed in a porcelain tube, gave the following results:—

	I.	II.	III.
Carbon .....	97·01	96·12	96·37
Hydrogen .....	..	0·12	0·18
Ash .....	4·88	4·87	3·99
	101·89	101·11	100·54

It is probable that both in this graphite and in that of natural occurrence, the hydrogen is not essential, but arises from hygroscopic moisture. The residual ash contained porous particles consisting of sesquioxide of iron and silica, and also small pellets, covered externally with a layer of magnetic oxide of iron: these dissolved in hydrochloric acid, at first quietly, and afterwards with disengagement of hydrogen; and in the solution small blisters of graphite could be perceived. It is owing to the oxidation of the iron that the sum of the constituents in all cases exceeds 100.

‡ After some more naphtha had been added.

## II.—Experiments with Naphtha A. Glass 1. Temperature of the Air 19°·9—20°·0.

T.	T'.	t.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grms.		grm.	
52·1	21·9	21·57	19·32	26·94	2·48	2·205	0·431	0·651	0·164
51·7	22·0	21·66	19·45	26·97	„	„	„	„	0·163
51·5	22·0	21·73	19·54	26·98	„	„	„	„	0·162
51·5	22·0	21·66	19·46	26·945	„	2·19*	„	„	0·167
Mean ..									0·164

The average of the means of both these series of experiments, 0·167 and 0·164, gives, as the specific heat of iron graphite between 22° and 52°, the number 0·166.

The results previously known with reference to the specific heat of carbon differ greatly for its different conditions, as also do the results obtained by different inquirers and by different methods for the same condition. But even leaving out of consideration the numbers obtained by De la Rive and Marcet by the method of cooling, there are still considerable differences between Regnault's results, obtained by the method of mixture, and my own. Regnault found, for animal charcoal 0·261, for wood-charcoal 0·241, for gas-carbon 0·209, for natural graphite 0·202, for iron graphite 0·197, for diamond 0·1469; his experiments gave greater numbers for the same substance than my own. I think that, exactly for a substance like carbon in its less dense modifications, my method promises more accurate results than that of Regnault. Even in mine, the substance, after being strongly heated before the experiment, might absorb gases or aqueous vapour, which would make the specific heat too great. But in Regnault's method, this source of error might also operate, and more especially also the source of error due to the disengagement of heat when porous substances are moistened by water. These sources of error, which affect the determination of the specific heat of the various modifications of carbon and make it too high, have the more influence the looser and the more porous the substance investigated. I believe that the only certain determination of the specific heat of carbon is that of diamond, and all other determinations are too high, owing to various circumstances, and in Regnault's experiments with wood and animal charcoal, &c., to the heat disengaged when these substances are moistened by water.

\* After drying the stopper.

37. *Silicium*.—I have investigated this substance in four different modifications.

*Amorphous Silicium*\*.—For the experiments, picked coherent pieces were used, which had stood for several days *in vacuo* over sulphuric acid.

Experiments with Naphtha A. Glass 3. Temperature of the Air 19°·2.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grm.	grms.		grm.	
51·5	20·7	20·38	18·13	26·95	1·095	2·88	0·431	0·453	0·251
50·0	20·8	20·54	18·46	26·975	"	"	"	"	0·208
50·4	21·0	20·66	18·55	26·98	"	"	"	"	0·221
50·5	20·9	20·59	18·52	26·935	"	2·87†	"	"	0·177
Mean ..									0·214

The very discordant results of these experiments are very little trustworthy; the quantity of silicium, 1 grm., was too small, and its thermal action inconsiderable as compared with that of the other substances immersed with it in the water of the calorimeter.

*Graphitoid Silicium*.‡

Experiments with Naphtha A. Glass 3. Temperature of the Air 16°·7—17°·2.

T.	T'.	t'.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
51·0	18·8	18·51	16·34	26·965	3·155	1·83	0·431	0·453	0·182
52·3	19·1	18·82	16·59	26·975	"	"	"	"	0·181
51·1	18·9	18·62	16·44	26·98	"	"	"	"	0·185
50·4	18·8	18·52	16·43	26·95	"	1·81†	"	"	0·174
Mean ..									0·181

*Crystallised Silicium*.—Grey needles.§

\* "Prepared from silicofluoride of potassium by means of sodium."—Wöhler.

† After drying the stopper.

‡ "Obtained by melting silicofluoride of potassium, or sodium, with aluminium; the aluminium was then extracted with hot hydrochloric acid, and the oxide of silicium with fluoric acid."—Wöhler.

§ "This silicium was prepared from the silicofluoride of potassium, or sodium, by sodium and zinc, and the lead (from the zinc) removed by nitric acid. Whether it was afterwards treated with hydrofluoric acid I cannot say, but probably so. It was quite unchanged when heated in the vapour of hydrochlorate of chloride of silicium (passed by means of hydrogen). Probably it contained, however, like all silicium reduced by zinc, a trace of iron, which appears when it is heated in chlorine. An experiment with another portion of such silicium gave, however, so little iron that its quantity could not be determined."—Wöhler.

Experiments with Naphtha A. Glass 1. Temperature of the Air  
19° 1.

T.	T'.	t.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
53·8	21·1	20·83	18·53	26·94	2·395	1·955	0·431	0·651	0·168
52·6	21·0	20·74	18·52	26·975	"	"	"	"	0·168
52·3	21·0	20·72	18·52	26·98	"	"	"	"	0·168
51·9	21·0	20·66	18·53	26·975	"	1·935*	"	"	0·156
Mean ..									0·165

*Fused Silicium.*†Experiments with Naphtha A. Glass 1. Temperature of the Air  
18° 9—18·7.

T.	T'.	t.	t.	M.	m.	f.	y.	x.	sp. H.
°	°	°	°	grms.	grms.	grm.		grm.	
49·0	20·5	20·24	18·40	26·97	4·17	1·555	0·431	0·651	0·142
50·5	20·7	20·43	18·52	26·96	"	"	"	"	0·139
49·7	20·6	20·27	18·42	26·965	"	"	"	"	0·136
50·8	20·7	20·43	18·52	26·94	"	1·145*	"	"	0·136
Mean ..									0·138

\* \* \* \* \*

PART IV.—*Table of the Substances whose Specific Heat has been experimentally determined.*

81. The determinations given in the following summary are principally due to Dulong and Petit (D. P.), Neumann (N.), Regnault (R.), and Kopp (Kp.). There are besides some of Person (Pr.), of Alluard (A.), and the recent investigations of Pape (Pp.) are also included. By far the largest number of these determinations have been made by the method of mixture. A few only of the elements investigated by Dulong and Petit, and some of the chemical compounds by Neumann were determined by the method of cooling. Where it is not otherwise stated in reference to the temperature, all determinations refer to temperatures between 0° and 100°. Where the determination has been made beyond these limits, or where a more accurate statement of temperature is important, it is noticed. Where the same substance has been repeatedly investigated by the same observer, the result obtained for the purer preparation, and in general the most certain result, is taken.

\* After drying the stopper.

† Wöhler had obtained it from Deville; it formed a cylindrical piece.

In the following tables, the chemical formula is given for each substance (the symbols used both here and subsequently, when not otherwise mentioned, referring to the numbers given in the last column of § 2 as the most recent assumptions for the atomic weights), also the corresponding atomic weight, and the atomic heat, viz., the product of the specific heat and the atomic weight.

82. *Elements and Alloys.*

		Atomic weight.		Specific heat.	Atomic heat.
Ag	..	108	{ .. .. .. ..	0·0557 D. P.	6·02
			{ .. .. .. ..	0·0570 R.	6·16
			{ .. .. .. ..	0·0560 Kp.	6·05
Al	..	27·4	{ .. .. .. ..	0·2143 R.	5·87
			{ .. .. .. ..	0·202 Kp.	5·53
As	..	75	{ .. .. .. ..	0·0814 R.	6·11
Au	..	197	{ .. .. .. ..	0·0298 D. P.	5·88
			{ .. .. .. ..	0·0324 R.	6·38
			{ Amorphous .. ..	0·254 Kp.	2·77
			{ Graphitoidal .. ..	0·235 R.	2·56
B..	..	10·9	{ Crystalline .. ..	0·230 Kp.	2·51
			{ " .. ..	0·225-0·262 R.	2·45-2·86
			{ .. .. .. ..	0·0288 D. P.	6·05
Bi..	..	210	{ .. .. .. ..	0·0308 R.	6·47
			{ .. .. .. ..	0·0305 Kp.	6·41
Br	..	80	{ Between -78° and 20° .. ..	0·0843 R.	6·74
			{ Wood charcoal .. ..	0·241 R.	2·89
			{ Gas carbon .. ..	0·204 R.	2·45
			{ " .. ..	0·185 Kp.	2·22
C..	..	12	{ Natural graphite .. ..	0·202 R.	2·42
			{ " .. ..	0·174 Kp.	2·09
			{ Iron graphite .. ..	0·197 R.	2·36
			{ " .. ..	0·166 Kp.	1·99
			{ Diamond .. ..	0·1469 R.	1·76
Cd	..	112	{ .. .. .. ..	0·0567 R.	6·35
			{ .. .. .. ..	0·0542 Kp.	6·07
Co	..	58·8	{ .. .. .. ..	0·1067 R.	6·27
			{ .. .. .. ..	0·0949 D. P.	6·02
Cu	..	63·4	{ Hammered .. ..	0·0935 R.	5·93
			{ Heated .. ..	0·0952 R.	6·04
			{ .. .. .. ..	0·0930 Kp.	5·90
			{ .. .. .. ..	0·1100 D. P.	6·16
Fe	..	56	{ .. .. .. ..	0·1138 R.	6·37
			{ .. .. .. ..	0·112 Kp.	6·27
			{ Between -78° and -40° .. ..	0·0319 R.	6·38
Hg	..	200	{ .. .. .. ..	0·0541 R.	6·87
I..	..	127	{ .. .. .. ..	0·0326 R.	6·45
Ir..	..	198	{ .. .. .. ..	0·1655 R.	6·47
K..	..	39·1	{ Between -78° and ? .. ..	0·9408 R.	6·59
Li..	..	7	{ .. .. .. ..	0·2499 R.	6·00
			{ .. .. .. ..	0·245 Kp.	5·88
Mg	..	24	{ .. .. .. ..	0·1217 R.	6·69
Mn	..	55	{ .. .. .. ..	0·0722 R.	6·93
Mo	..	96	{ .. .. .. ..	0·2934 R.	6·75
Na	..	23	{ Between -34° and 7° .. ..	0·1092 R.	6·42
Ni	..	58·8	{ .. .. .. ..	0·0311 R.	6·20
Os	..	199·2	{ .. .. .. ..		

	Atomic weight.		Specific heat.	Atomic heat.
P .. .. .	31	Yellow, between 13° and 36° ..	0.202 Kp.	6.26
		" " 7° " 30° ..	0.1895 R.	5.87
		" " -21° " 7° ..	0.1788 Pr.	5.54
		" " -78° " 10° ..	0.1740 R.	5.39
		Red " " 15° " 98° ..	0.1698 R.	5.26
Pb .. .. .	207	" " " " " " ..	0.0293 D. P.	6.06
		" " " " " " ..	0.0314 R.	6.50
		" " " " " " ..	0.0315 Kp.	6.52
Pd .. .. .	106.6	" " " " " " ..	0.0593 R.	6.32
		" " " " " " ..	0.0314 D. P.	6.20
Pt.. .. .	197.4	" " " " " " ..	0.0324 R.	6.40
		" " " " " " ..	0.0325 Kp.	6.42
Rh .. .. .	104.4	" " " " " " ..	0.0580 R.	6.06
		" " " " " " ..	0.1880 D. P.	6.02
S .. .. .	32	Rhombic, between 14° and 99°	0.1776 R.	5.68
		" " " 17° " 45° ..	0.163 Kp.	5.22
Sb .. .. .	122	" " " " " " ..	0.0507 D. P.	6.20
		" " " " " " ..	0.0508 R.	6.20
		" " " " " " ..	0.0523 Kp.	6.38
Se.. .. .	79.4	Amorphous, bet. -27° and 8°	0.0746 R.	5.92
		Crystalline, " 98° " 20°	0.0762 R.	6.05
		" " -18° " 7°	0.0745 R.	5.92
		Graphitoidal " " " " ..	0.181 Kp.	5.07
Si.. .. .	28	Crystallised " " " " ..	0.165 Kp.	4.62
		Fused " " " " ..	0.167-0.179 R.	4.68-5.01
		" " " " " " ..	0.138 Kp.	3.86
Sn .. .. .	118	" " " " " " ..	0.156-0.175 R.	4. -4.90
		" " " " " " ..	0.0514 D. P.	6.06
		" " " " " " ..	0.0562 R.	6.63
Te .. .. .	128	" " " " " " ..	0.0548 Kp.	6.46
		" " " " " " ..	0.0474 R.	6.07
Tl.. .. .	204	" " " " " " ..	0.0475 Kp.	6.08
		" " " " " " ..	0.0336 R.	6.85
W.. .. .	184	" " " " " " ..	0.0334 R.	6.15
		" " " " " " ..	0.0927 D. P.	6.04
Zn .. .. .	65.2	" " " " " " ..	0.0956 R.	6.23
		" " " " " " ..	0.0932 Kp.	6.08

*Alloys which only melt far above 100°.*

Bi Sn .. .. .	328	" " " " " " ..	0.0400 R.	13.1
Bi Sn <sub>2</sub> .. .. .	446	" " " " " " ..	0.0450 R.	20.1
Bi Sn <sub>2</sub> Sb .. .. .	568	" " " " " " ..	0.0462 R.	26.2
Bi Sn <sub>2</sub> SbZn <sub>2</sub> .. .. .	698.4	" " " " " " ..	0.0566 R.	39.5
Pb Sb .. .. .	329	" " " " " " ..	0.0388 R.	12.8
Pb Sn .. .. .	325	" " " " " " ..	0.0407 R.	13.2
Pb Sn <sub>2</sub> .. .. .	443	" " " " " " ..	0.0451 R.	20.0

*83. Arsenides and Sulphides.*

Co As <sub>2</sub> .. .. .	208.8	Speis-cobalt .. .. .	0.0920 N.	19.2
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As the locality of this mineral is not given, the formula and atomic weight are not certain. Metals replacing the cobalt can, however, have little influence on the atomic weight and the product.



	Atomic weight.		Specific heat.	Atomic heat.
Ag <sub>2</sub> S .. ..	248	Fused .. ..	0·0746 R.	18·5
Co As S .. ..	166	Cobalt-glance .. ..	0·1070 N.	17·8
Cu <sub>2</sub> S .. ..	158·8	{ Fused .. ..	0·1212 R.	19·2
		{ Copper-glance .. ..	0·120 Kp.	19·1
Fe As S .. ..	163	Mispickel .. ..	0·1012 N.	16·5
As S .. ..	107	Commercial .. ..	0·1111 N.	11·9
Co S .. ..	90·8	Fused .. ..	0·1251 R.	11·4
Cu $\frac{1}{2}$ Fe $\frac{3}{4}$ S .. ..	91·7	{ Copper pyrites .. ..	0·1289 N.	11·8
		{ Fused " .. ..	0·131 Kp.	12·1
Fe S .. ..	88	{ Fused " .. ..	0·1357 R.	11·9
		{ Cinnabar .. ..	0·052 N.	12·1
Hg S .. ..	232	{ " .. ..	0·0512 R.	11·9
		{ " .. ..	0·0517 Kp.	12·0
Ni S .. ..	90·8	Fused .. ..	0·1281 R.	11·6
		{ Galena .. ..	0·053 N.	12·7
Pb S .. ..	239	{ " .. ..	0·0509 R.	12·2
		{ " .. ..	0·0490 Kp.	11·7
Sn S .. ..	150	Fused .. ..	0·0837 R.	12·6
		{ Zinc-blende .. ..	0·1145 N.	11·1
Zn S .. ..	97·2	{ " .. ..	0·1230 R.	12·0
		{ " .. ..	0·120 Kp.	11·7
Fe <sub>7</sub> S <sub>8</sub> .. ..	648	{ Magnetic pyrites .. ..	0·1533 N.	99·3
		{ " .. ..	0·1602 R.	103·8
As <sub>2</sub> S <sub>3</sub> .. ..	246	Natural .. ..	0·1132 N.	27·8
Bi <sub>2</sub> S <sub>3</sub> .. ..	516	Artificial .. ..	0·0600 R.	31·0
Sb <sub>2</sub> S <sub>3</sub> .. ..	340	{ Natural .. ..	0·0907 N.	30·8
		{ Artificial .. ..	0·0840 R.	28·6
		{ Marcasite .. ..	0·1332 N.	16·0
Fe S <sub>2</sub> .. ..	120	{ Iron pyrites .. ..	0·1275 N.	15·3
		{ " .. ..	0·1301 R.	15·6
		{ " .. ..	0·126 Kp.	15·1
Mo S <sub>2</sub> .. ..	160	{ Natural .. ..	0·1067 N.	17·1
		{ " .. ..	0·1233 R.	19·7
Sn S <sub>2</sub> .. ..	182	Aurum musivum .. ..	0·1193 R.	21·7

## 84. Chlorine, Bromine, Iodine, and Fluorine Compounds.

Ag Cl .. ..	143·5	Fused .. ..	0·0911 R.	13·1
Cu Cl .. ..	98·9	" .. ..	0·1383 R.	13·7
Hg Cl .. ..	235·5	Sublimed .. ..	0·0521 R.	12·3
K Cl .. ..	74·6	{ Fused .. ..	0·1730 R.	12·9
		{ " .. ..	0·171 Kp.	12·8
Li Cl .. ..	42·5	" .. ..	0·2821 R.	12·0
		" .. ..	0·2140 R.	12·5
Na Cl .. ..	58·5	" .. ..	0·213 Kp.	12·5
		{ Rock-salt .. ..	0·219 Kp.	12·8
Rb Cl .. ..	120·9	Fused .. ..	0·112 Kp.	13·5
N H <sub>4</sub> Cl .. ..	53·5	Crystallised .. ..	0·373 Kp.	20·0
Ba Cl <sub>2</sub> .. ..	208	{ Fused .. ..	0·0896 R.	18·6
		{ " .. ..	0·0902 Kp.	18·8
Ca Cl <sub>2</sub> .. ..	111	" .. ..	0·1642 R.	18·2
Hg Cl <sub>2</sub> .. ..	271	{ Sublimed .. ..	0·0689 R.	18·7
		{ Crystallised .. ..	0·0640 Kp.	17·3
Mg Cl <sub>2</sub> .. ..	95	{ Fused .. ..	0·1946 R.	18·5
		{ " .. ..	0·191 Kp.	18·2
Mn Cl <sub>2</sub> .. ..	126	" .. ..	0·1425 R.	18·0
Pb Cl <sub>2</sub> .. ..	278	" .. ..	0·0664 R.	18·5
Sn Cl <sub>2</sub> .. ..	189	" .. ..	0·1016 R.	19·2

	Atomic weight.		Specific heat.	Atomic heat.
Sr Cl <sub>2</sub> .. ..	158.6	Fused .. ..	0.1199 R.	19.0
Zn Cl <sub>2</sub> .. ..	136.2	" .. ..	0.1362 R.	18.6
Ba Cl <sub>2</sub> . 2 H <sub>2</sub> O ..	244	Crystallised .. ..	0.171 Kp.	41.7
Ca Cl <sub>2</sub> . 6 H <sub>2</sub> O ..	219	Between -21° and 0° ..	0.345 Pr.	75.6
Zn K <sub>2</sub> Cl <sub>4</sub> .. ..	285.4	Crystallised .. ..	0.152 Kp.	43.4
Pt K <sub>2</sub> Cl <sub>6</sub> .. ..	488.6	" .. ..	0.113 Kp.	55.2
Sn K <sub>2</sub> Cl <sub>6</sub> .. ..	409.2	" .. ..	0.133 Kp.	54.4
Cr <sub>2</sub> Cl <sub>6</sub> .. ..	317.4	" .. ..	0.143 Kp.	45.4
Ag Br .. ..	188	Fused .. ..	0.0739 R.	13.9
K Br .. ..	119.1	" .. ..	0.1132 R.	13.5
Na Br .. ..	103	"* .. ..	0.1384 R.	14.3
Pb Br <sub>2</sub> .. ..	367	" .. ..	0.0533 R.	19.6
Ag I .. ..	235	" .. ..	0.0616 R.	14.5
Cu I .. ..	190.4	" .. ..	0.0687 R.	13.1
Hg I .. ..	327	Powder .. ..	0.0395 R.	12.9
K I .. ..	166.1	Fused .. ..	0.0819 R.	13.6
Na I .. ..	150	" .. ..	0.0868 R.	13.0
Hg I <sub>2</sub> .. ..	454	" .. ..	0.0420 R.	19.1
Pb I <sub>2</sub> .. ..	461	" .. ..	0.0427 R.	19.7
Ca Fl <sub>2</sub> .. ..	78	{ Fluor-spar .. ..	0.2082 N.	16.2
		{ " .. ..	0.2149 R.	16.8
		{ " .. ..	0.209 Kp.	16.3
Al Na <sub>3</sub> Fl <sub>6</sub> .. ..	210.4	{ Cryolite .. ..	0.238 Kp.	50.1
Cu <sub>2</sub> O .. ..	142.8	{ Red copper ore .. ..	0.1073 N.	15.3
		{ " .. ..	0.111 Kp.	15.9
H <sub>2</sub> O .. ..	18	{ Ice between -21° and -2° ..	0.480 Pr.	8.6
		{ " 78° " 0° ..	0.474 R.	8.5

Desains found the specific heat of ice between -20° and 0° to be 0.513; Person, between -20° and 0° = 0.504; Hess, between -14° and 0° = 0.533. Person is of opinion that ice even somewhat below its melting-point, between -2° and 0°, absorbs heat of fusion.

Cu O .. ..	79.4	{ .. ..	0.137 N.	10.9
		{ .. ..	0.1420 R.	11.3
		{ .. ..	0.128 Kp.	10.2
Hg O .. ..	216	{ Commercial .. ..	0.049 N.	10.6
		{ Crystalline .. ..	0.0518 R.	11.2
		{ " .. ..	0.0530 Kp.	11.4
Mg O .. ..	40	{ .. ..	0.276 N.	11.0
		{ .. ..	0.2439 R.	9.8
Mn O .. ..	71	{ .. ..	0.1570 R.	11.1
Ni O .. ..	74.8	{ Feebly ignited .. ..	0.1623 R.	12.1
		{ Strongly ignited .. ..	0.1588 R.	11.9
		{ Fused .. ..	0.0509 R.	11.4
Pb O .. ..	223	{ Crystalline powder .. ..	0.0512 R.	11.4
		{ " .. ..	0.0553 Kp.	12.3
Zn O .. ..	81.2	{ .. ..	0.132 N.	10.7
		{ .. ..	0.1248 R.	10.1
Mg O . H <sub>2</sub> O .. ..	58	{ Brucite .. ..	0.312 Kp.	18.1
		{ Magnetic iron ore .. ..	0.1641 N.	38.1
Fe <sub>3</sub> O <sub>4</sub> .. ..	232	{ " .. ..	0.1678 R.	38.9
		{ " .. ..	0.156 Kp.	36.2
Mg Al <sub>2</sub> O <sub>4</sub> .. ..	142.8	{ Spinelle .. ..	0.194 Kp.	27.7
Mg $\frac{1}{2}$ Fe $\frac{1}{2}$ Cr $\frac{3}{2}$ Al $\frac{1}{2}$ O <sub>4</sub> ..	196	{ Chrome iron ore .. ..	0.159 Kp.	31.2

\* The preparation contained carbonate of sodium.

	Atomic weight.		Specific heat.	Atomic heat.
$Al_2 O_3$ .. ..	102·8	Sapphire .. ..	0·1972 N.	20·3
			0·2173 R.	22·3
$As_2 O_3$ .. ..	198	Opaque .. ..	0·1279 R.	25·3
$B_2 O_3$ .. ..	69·8	Fused .. ..	0·2374 R.	16·6
$Bi_2 O_3$ .. ..	468	.. ..	0·0605 R.	28·3
$Cr_2 O_3$ .. ..	152·4	.. ..	0·196 N.	29·9
			0·1796 R.	27·4
			0·177 Kp.	27·0
			0·1757 R.	28·1
$Fe_2 O_3$ .. ..	160	Artificial, feebly ignited " strongly ignited Specular iron .. ..	0·1681 R.	26·9
			0·1692 N.	27·1
			0·1670 R.	26·7
			0·154 Kp.	25·1
$Fe_3 Ti_3^{\frac{3}{4}} O_3$ .. ..	155·5	Iserine .. ..	0·1762 N.	27·4
			0·177 Kp.	27·5
$Sb_2 O_3$ .. ..	292	Fused .. ..	0·0901 R.	26·3
$Mn_2 O_3 \cdot H_2 O$ .. ..	176	Manganite .. ..	0·176 Kp.	31·0
$Mn O_2$ .. ..	87	Pyrolusite .. ..	0·159 Kp.	13·8
$Si O_2$ .. ..	60	Quartz .. ..	0·1883 N.	11·3
			0·1913 R.	11·5
			0·186 Kp.	11·2
$Si_2 Zr_2 O_2$ .. ..	90·8	Zircon .. ..	0·1456 R.	13·2
			0·132 Kp.	12·0
			0·0931 N.	14·0
$Sn O_2$ .. ..	150	Cassiterite .. ..	0·0933 R.	14·0
			0·0894 Kp.	13·4
			0·1716 R.	14·1
$Ti O_2$ .. ..	82	Artificial Rutile .. ..	0·1724 N.	14·1
			0·1703 R.	14·0
			0·157 Kp.	12·9
			0·161 Kp.	13·2
$Mo O_3$ .. ..	144	Fused .. ..	0·1324 R.	19·1
			0·154? Kp.	22·2
			0·0798 R.	18·5
$W O_3$ .. ..	232	Pulverulent .. ..	0·0894? Kp.	20·7
			.. ..	.. ..

## 86. Carbonates and Silicates.

$K_2 C O_3$ .. ..	138·2	Fused .. ..	0·2162 R.	29·9
			0·206 Kp.	28·5
$Na_2 C O_3$ .. ..	106	" .. ..	0·2728 R.	28·9
			0·246 Kp.	26·1
$Rb_2 C O_3$ .. ..	230·8	" .. ..	0·123 Kp.	28·4
			0·1078 N.	21·2
$Ba C O_3$ .. ..	197	Witherite .. ..	0·1104 R.	21·7
			0·2046 N.	20·5
			0·2086 R.	20·9
			0·206 Kp.	20·6
$Ca C O_3$ .. ..	100	Arragonite .. ..	0·2018 N.	20·2
			0·2085 R.	20·9
			0·203 Kp.	20·3
			0·2161 N.	19·9
$Ca_2 Mg_2 C O_3$ .. ..	92	Bitter spar .. ..	0·2179 R.	20·0
			0·206 Kp.	19·0
$Fe C O_3$ .. ..	116	Spathic iron .. ..	0·182 N.	21·1
			0·1934 R.	22·4

The minerals investigated doubtless contained part of the iron

replaced by metals of lower atomic weight. The atomic weight and the product assumed above are somewhat too great.

	Atomic weight.		Specific heat.	Atomic heat.
$F_{\frac{4}{1}} Mn_{\frac{2}{1}} Mg_{\frac{1}{1}} CO_3$	112·9	Spathic iron .. ..	0·166 Kp.	18·7
$Mg_{\frac{2}{1}} Fe_{\frac{2}{1}} C O_3$ ..	91·1	Magnesite .. ..	0·227 N.	20·7
$Pb C O_3$ .. ..	267	{ Cerussite .. ..	0·0814 N.	21·7
		{ " .. ..	0·0791 Kp.	21·1

Regnault found for precipitated carbonate of lead still containing water, the specific heat 0·0860.

$Sr C O_3$ .. ..	147·6	{ Strontianite .. ..	0·1445 N.	21·3
		{ Artificial .. ..	0·1448 R.	21·4
$Ca Si O_3$ .. ..	116	Wollastonite .. ..	0·178 Kp.	20·7
$Ca_{\frac{2}{1}} Mg_{\frac{1}{1}} Si O_3$ ..	108	{ Diopside from Tyrol .. ..	0·1906 N.	20·6
		{ " .. ..	0·186 Kp.	20·1
$Cu Si O_3 \cdot H_2 O$ ..	157·4	Diopside .. ..	0·182 Kp.	28·7
		Olivine .. ..	0·189 Kp.	27·6
$Mg_{\frac{2}{1}} Fe_{\frac{2}{1}} Si O_4$	145·8	Crysolite .. ..	0·189 Kp.	27·6
		{ " .. ..	0·2056 N.	30·0
		{ Adularia .. ..	0·1861 N.	103·7
$Al_2 K_2 Si_6 O_{16}$ ..	557	{ Orthoclase .. ..	0·1911 N.	106·4
		{ " .. ..	0·183 Kp.	101·9
$Al_2 Na_2 Si_6 O_{16}$ ..	524·8	{ Albite .. ..	0·1961 N.	102·9
		{ " .. ..	0·190 Kp.	99·7

### 87. Borates, Molybdates, Tungstates, Chromates, and Sulphates.

$K B O_2$ .. ..	82	Fused .. ..	0·2048 R.	16·8
$Na B O_2$ .. ..	65·9	" .. ..	0·2571 R.	16·9
$Pb B_2 O_4$ .. ..	292·8	" .. ..	0·0905 R.	26·5
$Pb B_4 O_7$ .. ..	362·6	" .. ..	0·1141 R.	41·4
$K_2 B_4 O_7$ .. ..	233·8	" .. ..	0·2198 R.	51·4
$Na_2 B_4 O_7$ .. ..	201·6	{ " .. ..	0·2382 R.	48·0
		{ " .. ..	0·229 Kp.	46·2
$Na_2 B_4 O_7 \cdot 10H_2 O$	381·6	Crystallised borax .. ..	0·385 Kp.	146·9
$Pb Mo O_4$ .. ..	367	Yellow lead ore .. ..	0·0827 Kp.	30·4
$Ca W O_4$ .. ..	288	Scheelite .. ..	0·0967 Kp.	27·9
$Fe_{\frac{2}{1}} Mn_{\frac{2}{1}} W O_4$ ..	333·4	{ Tungsten .. ..	0·0930 Kp.	28·2
		{ " .. ..	0·0978 R.	29·7

The locality of the wolfram investigated by Regnault is not known, and the composition uncertain. But the change in the ratio in which iron and manganese are present in the mineral alters little in the atomic weight.

$Pb Cr O_4$ .. ..	323·4	Fused .. ..	0·0900 Kp.	29·0
$K_2 Cr O_4$ .. ..	194·4	{ Crystallised .. ..	0·1851 R.	36·0
		{ " .. ..	0·189 Kp.	36·7
$K_2 Cr_2 O_7$ .. ..	294·6	{ " .. ..	0·1894 R.	55·8
		{ " .. ..	0·186 Kp.	54·8
$K H S O_4$ .. ..	136·1	" .. ..	0·244 Kp.	33·2

	Atomic weight.		Specific heat.	Atomic heat.
K <sub>2</sub> S O <sub>4</sub> ..	174·2	Fused .. .. .	0·1901 R.	33·1
		Crystallised .. .. .	0·196 Kp.	34·1
Na <sub>2</sub> S O <sub>4</sub> ..	142	Fused .. .. .	0·2312 R.	32·3
		Crystallised .. .. .	0·227 Kp.	32·2
Na <sub>2</sub> H <sub>8</sub> S O <sub>4</sub> ..	132	" .. .. .	0·350 Kp.	46·2
Ba S O <sub>4</sub> ..	233	Heavy spar .. .. .	0·1088 N.	25·4
		" .. .. .	0·1128 R.	26·3
		" .. .. .	0·108 Kp.	25·2
		Calcined gypsum .. .. .	0·1966 R.	26·7
Ca S O <sub>4</sub> ..	136	Anhydrite .. .. .	0·1854 N.	25·2
		" .. .. .	0·178 Kp.	24·2
Cu S O <sub>4</sub> ..	159·4	Solid pieces .. .. .	0·184 Pp.	29·3
Mg S O <sub>4</sub> ..	120	Dehydrated salt .. .. .	0·2216 R.	26·6
		Solid pieces .. .. .	0·225 Pp.	27·0
Mn S O <sub>4</sub> ..	151	" .. .. .	0·182 Pp.	27·5
Pb S O <sub>4</sub> ..	303	Artificial .. .. .	0·0872 R.	26·4
		Lead-vitriol .. .. .	0·0848 N.	25·7
		" .. .. .	0·0827 Kp.	25·1
		Artificial .. .. .	0·1428 R.	26·2
Sr S O <sub>4</sub> ..	183·6	Cœlestine .. .. .	0·1356 N.	24·9
		" .. .. .	0·135 Kp.	24·8
Zn S O <sub>4</sub> ..	161·2	Coarse powder .. .. .	0·174 Pp.	28·0
Cu S O <sub>4</sub> · H <sub>2</sub> O ..	177·4	Pulverulent .. .. .	0·202 Pp.	35·8
Mg S O <sub>4</sub> · H <sub>2</sub> O ..	138	Coarse powder .. .. .	0·264 Pp.	36·4
Zn S O <sub>4</sub> · H <sub>2</sub> O ..	179·2	Solid pieces .. .. .	0·202 Pp.	36·2
		Gypsum .. .. .	0·2728 N.	46·9
Cu S O <sub>4</sub> · 2 H <sub>2</sub> O ..	172	" .. .. .	0·259 Kp.	44·6
Cu S O <sub>4</sub> · 2 H <sub>2</sub> O ..	195·4	Pulverulent .. .. .	0·212 Pp.	41·4
Zn S O <sub>4</sub> · 2 H <sub>2</sub> O ..	197·2	Solid pieces .. .. .	0·224 Pp.	44·2
Fe S O <sub>4</sub> · 3 H <sub>2</sub> O ..	206	" .. .. .	0·247 Pp.	50·9
Cu S O <sub>4</sub> · 5 H <sub>2</sub> O ..	249·4	Crystallised .. .. .	0·285 Kp.	71·1
		" .. .. .	0·316 Pp.	78·8
		" .. .. .	0·323 Kp.	77·8
		" .. .. .	0·338 Pp.	81·5
Ni S O <sub>4</sub> · 6 H <sub>2</sub> O ..	262·8	" .. .. .	0·313 Kp.	82·3
Co S O <sub>4</sub> · 7 H <sub>2</sub> O ..	280·8	" .. .. .	0·343 Kp.	96·4
Fe S O <sub>4</sub> · 7 H <sub>2</sub> O ..	278	" .. .. .	0·346 Kp.	96·2
		" .. .. .	0·356 Pp.	99·0
Mg S O <sub>4</sub> · 7 H <sub>2</sub> O ..	246	" .. .. .	0·362 Kp.	89·1
		" .. .. .	0·407 Pp.	100·1
Zn S O <sub>4</sub> · 7 H <sub>2</sub> O ..	287·2	" .. .. .	0·347 Kp.	99·7
		" .. .. .	0·328 Pp.	94·2
MgK <sub>2</sub> S <sub>2</sub> O <sub>8</sub> · 6H <sub>2</sub> O	402·2	" .. .. .	0·264 Kp.	106·2
NiK <sub>2</sub> S <sub>2</sub> O <sub>8</sub> · 6H <sub>2</sub> O	437	" .. .. .	0·245 Kp.	107·1
ZnK <sub>2</sub> S <sub>2</sub> O <sub>8</sub> · 6H <sub>2</sub> O	443·4	" .. .. .	0·270 Kp.	119·7
Al <sub>2</sub> K <sub>2</sub> S <sub>4</sub> O <sub>16</sub> · 24H <sub>2</sub> O	949	" alum .. .. .	0·371 Kp.	352·1
Cr <sub>2</sub> K <sub>2</sub> S <sub>4</sub> O <sub>16</sub> · 24H <sub>2</sub> O	998·6	" chrome alum .. .. .	0·324 Kp.	323·6

88. *Arsenates, Phosphates, Pyrophosphates and Metaphosphates, Nitrates, Chlorates, Perchlorates, and Permanganates.*

K As O <sub>3</sub> ..	162·1	Fused .. .. .	0·1563 R.	25·3
K H <sub>2</sub> As O <sub>4</sub> ..	180·1	Crystallised .. .. .	0·175 Kp.	31·5
Pb <sub>3</sub> As <sub>2</sub> O <sub>8</sub> ..	899	Fused .. .. .	0·0728 R.	65·4
Ag <sub>3</sub> P O <sub>4</sub> ..	419	Pulverulent .. .. .	0·0896? Kp.	37·5
K H <sub>2</sub> P O <sub>4</sub> ..	136·1	Crystallised .. .. .	0·280 Kp.	28·3
Na <sub>2</sub> HPO <sub>4</sub> · 12H <sub>2</sub> O	358	Between - 21° and 22° .. .. .	0·408 Pr.	146·1

The determination of the specific heat refers to the crystallised salt. For the fused and afterwards solidified salt Person found the specific heat between the same range of temperature considerably greater, = 0.68 to 0.78; but the mass obtained by solidifying the fused salt gradually alters (it becomes crystallised again) with increase of volume, which is very considerable when the fused salt is allowed to cool very rapidly.

	Atomic weight.		Specific heat.	Atomic heat.
Pb <sub>3</sub> P <sub>2</sub> O <sub>8</sub>	811	.. .. .	0.0798 R.	64.7
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ..	330.4	Fused .. .. .	0.1910 R.	63.1
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	266	" .. .. .	0.2283 R.	60.7
Pb <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	588	" .. .. .	0.0821 R.	48.3
Na P O <sub>3</sub> ..	102	" .. .. .	0.217 Kp.	22.1
Ca P <sub>2</sub> O <sub>6</sub> ..	198	" .. .. .	0.1992 R.	39.4
Ag N O <sub>3</sub> ..	170	" .. .. .	0.1435 R.	24.4
K N O <sub>3</sub> ..	101.1	" .. .. .	0.2388 R.	24.1
		" Crystallised .. .. .	0.227 Kp.	22.9
K <sub>1/2</sub> Na <sub>1/2</sub> N O <sub>3</sub>	93	Fused* .. .. .	0.232 Kp.	28.5
		" .. .. .	0.235 Pr.	21.9
Na N O <sub>3</sub> ..	85	" .. .. .	0.2782 R.	23.6
		" Crystallised .. .. .	0.256 Kp.	21.8
N <sub>2</sub> H <sub>4</sub> O <sub>3</sub> ..	80	" .. .. .	0.257 Kp.	21.8
Ba N <sub>2</sub> O <sub>6</sub> ..	261	" .. .. .	0.455 Kp.	36.4
Pb N <sub>2</sub> O <sub>6</sub> ..	331	" .. .. .	0.1523 R.	39.8
Sr N <sub>2</sub> O <sub>6</sub> ..	211.6	" .. .. .	0.145 Kp.	37.9
K Cl O <sub>3</sub> ..	122.6	Fused .. .. .	0.110 Kp.	36.4
		" Crystallised .. .. .	0.181 Kp.	38.3
Ba Cl <sub>2</sub> O <sub>6</sub> . H <sub>2</sub> O	322	" .. .. .	0.2096 R.	25.7
K Cl O <sub>4</sub> ..	138.6	" .. .. .	0.194 Kp.	28.8
K Mn O <sub>4</sub>	158.1	" .. .. .	0.157 Kp.	50.6
			0.190 Kp.	26.3
			0.179 Kp.	28.3

### 89. So-called Organic Compounds.

Hg C <sub>2</sub> N <sub>2</sub>	252	Crystallised cyanide of mercury	0.100 Kp.	25.2
Zn K <sub>2</sub> C <sub>4</sub> N <sub>4</sub>	247.4	" cyanide of zinc and potassium .. .. .	0.241 Kp.	59.6
Fe K <sub>3</sub> C <sub>6</sub> N <sub>6</sub>	329.3	Crystallised ferricyanide of potassium .. .. .	0.233 Kp.	76.7
FeK <sub>4</sub> C <sub>6</sub> N <sub>6</sub> . 3H <sub>2</sub> O	422.4	Crystallised ferrocyanide of potassium .. .. .	0.280 Kp.	118.3
C <sub>2</sub> Cl <sub>6</sub>	237	Between 18° and 37° .. .. .	0.178 Kp.	42.2

The specific heat between 18° and 43° was found = 0.194; between 18° and 50° = 0.277.

C <sub>10</sub> H <sub>8</sub>	128	Between - 26° and 18° .. .. .	0.3096 A.	39.6
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\* Obtained as mass of constant melting-point (219°.8) by fusing equivalent quantities of nitrate of potass and nitrate of soda.

The specific heat of naphthalene was found to be 0.3208 between 0° and 20°, and 0.3208 between 20° and 65°.

	Atomic weight.		Specific heat.	Atomic heat.
$C_{27}H_{54}O_2$	.. 410	} Between - 21° and 3°	.. 0.4287 Pr.	} { 175.8 289.8
$C_{46}H_{92}O_2$	.. 676			

The first formula is that of one constituent of bees'-wax, cerotic acid; the second is that of the other, palmitate of melissyl. With reference to the numbers found for the specific heat of bees'-wax at higher temperatures, compare the last remark in § 77.

$C_{12}H_{22}O_{11}$	.. 342	} Crystallised cane-sugar .. 0.301 Kp. 102.9 Amorphous cane-sugar .. 0.342 Kp. 117.0
$C_6H_{14}O_6$	.. 182	
$C_4H_6O_4$ ..	.. 118	Mannite .. .. 0.324 Kp. 59.1
$C_4H_6O_6$ ..	.. 150	Succinic acid .. .. 0.313 Kp. 36.9
$C_4H_6O_6 \cdot H_2O$ ..	.. 168	Tartaric acid .. .. 0.288 Kp. 43.2
$C_2H_2BaO_4$ ..	.. 227	Racemic acid .. .. 0.319 Kp. 53.6
$C_2K_2O_4 \cdot H_2O$ ..	184.2	Formate of barium .. .. 0.143 Kp. 32.5
$C_4H_3KO_8 \cdot 2H_2O$	254.1	Neutral oxalate of potassium .. 0.236 Kp. 43.5
$C_4H_5KO_6$ ..	.. 188.1	Quadroxalate of potassium .. 0.283 Kp. 71.9
$C_4H_4NaKO_6 \cdot 4H_2O$	282.1	Acid tartrate of potassium .. 0.257 Kp. 48.3
$C_8H_{10}CaO_{10} \cdot 8H_2O$	450	Seignette salt .. .. 0.328 Kp. 92.5
		Acid malate of calcium .. 0.338 Kp. 152.1

The preceding tables contain the material, obtained experimentally, which serves as subject and basis for the subsequent considerations on the relations of the specific heat of solid bodies to their atomic weight and composition.

#### PART V.—On the Relations between Atomic Heat and Atomic Weight or Composition.

90. I discuss in the sequel the regularities exhibited by the atomic heats of solid bodies, the exceptions to these regularities, and the most probable explanation of these exceptions. With regard to the views which are here developed, much has been already expressed or indicated in former speculations; in this respect I refer to the first part of this paper, in which I have given the views of earlier inquirers as completely as I know them, and as fully as was necessary to bring out the peculiar value of each. It is unnecessary, then, to refer again to what was there given; but I will complete for individual special points what is to be remarked from an historical point of view.

But before discussing these regularities, the question must be discussed whether the atomic heat of a given solid substance is



essentially constant, or varies materially with its physical condition. It depends on the result of this investigation, how far it may with certainty be settled whether the general results already obtained are of universal validity, or whether exceptions to them exist.

The specific heat of a solid body varies somewhat with its temperature: but the variation of the specific heat with the temperature is very small, provided the latter does not rise so high that the body begins to soften. Taking the numbers obtained by Regnault for lead, by Dulong and Petit, by Bede and by Byström, for the specific heats of several metals at different temperatures, the conviction follows that the changes of specific heat, if not of themselves inconsiderable, are yet scarcely to be regarded in comparison with the discrepancies in the numbers which different observers have found for the specific heat of the same body at the same temperature. At temperatures at which a body softens, the specific heat does indeed vary considerably with the temperature (compare for example § 77); but these numbers, as containing already part of the latent heat of fusion, give no accurate expression for the specific heat, and are altogether useless for recognising the relations between this property and the atomic weight or composition.

Just as little need the small differences be considered which Regnault found for a few metallic substances according as they were hammered or annealed, hard or soft.

For dimorphous varieties of the same substance, even where there are considerable differences in the specific gravity, the specific heats have not been found to be materially different (see  $\text{FeS}_2$ , § 83;  $\text{TiO}_2$ , § 85;  $\text{CaCO}_3$ , § 86). The results obtained with these substances appear to me more trustworthy than those with graphite and the various modifications of boron and silicium, which moreover have given partly the same specific heat for the graphitoidal and adamantine modification of the same element. What trustworthy observations we now possess decidedly favour the view that the dimorphic varieties of the same substance have essentially the same specific heat.

91. It has been surmised that the same substance might have an essentially different specific heat in the amorphous and crystalline states. I believe that the differences of specific heat found for these different conditions depend, to by far the greatest extent, upon other circumstances.

The tables in § 83 to § 89 contain a tolerable number of substances which have been investigated both after being melted and also crystallised; there are no such differences in the numbers as to lead to the supposition that the amorphous solidified substance had a different specific heat to what it had in the crystallised state. No such influence of the state has been with any certainty shown to affect the validity of Dulong and Petit's, or of Neumann's law. I may here again neglect what the determinations of carbon, boron, or silicium appear to say for or against the assumption of a considerable influence of the amorphous or crystalline condition on the specific heat. Regnault found (§ 85) that the specific heat of artificially prepared (uncrystalline?) and crystallised titanitic acid did not differ. According to my investigations (§ 48), silicic acid has almost the same specific heat in the crystallised and in the amorphous condition.

In individual cases, where the specific heat of the same substance for the amorphous and crystallised modification has been found to be materially different\*, it may be shown that foreign influences affected the determination for the one condition. Such influences are especially: 1. That one modification absorbed heat of softening at the temperature of the experiment; that is doubtless the reason why the specific heat of yellow phosphorus was found to be considerably greater at higher temperatures than that of red phosphorus, but not at low temperatures (compare § 82), that the specific heat of amorphous cane-sugar was found to be decidedly greater than that of the crystallised variety (§ 78), and, according to Regnault's opinion, also that the specific heat of amorphous selenium between 80° and 18° was found much greater (= 0.103) than that of the crystalline, while for lower temperatures there was no difference in the specific heats of the two substances (§ 82). 2. That in heating one modification, its transition into the other is induced, and the heat liberated in this transition makes the numbers for the specific heat incorrect; in § 33 I have discussed the probability that this circumstance, in Regnault's first experiments with sulphur, gave the specific heat much too

\* De la Rive and Marcet (Ann. Ch. Phys. [2] lxxv, 118) found the specific heat of vitreous to be different from that of opaque arsenious acid, and considered the fact to be essential; but their method was not fitted to establish such a difference. Pape's view, too (Pogg. Ann. cxx, 341 and 342), that it is of essential importance for the specific heat of hydrated sulphates whether the salts are crystallized or not, does not appear to me to be proved by what he has adduced.

high, and it is possible that it was also perceptible in the above-mentioned experiments with amorphous selenium. 3. That in immersing heated porous bodies in the water of the calorimeter heat becomes free (compare § 19); I consider this as the reason why Regnault found the specific heat of the more porous forms of carbon so much greater than that of the more compact forms (compare § 36); and Regnault himself sees in this the reason why he found the specific heat of the feebly ignited and porous oxides of nickel and of iron greater than that of the same oxides after stronger heating (compare § 85).

From the importance of this subject for the considerations to be afterwards adduced, I have here had to discuss more fully what differences are real and what are only apparent in the numbers found for the specific heat of one and the same substance. Even if the apparent differences are often considerable, their importance diminishes, if allowance is made for the foreign influence which may have prevailed. In many cases, on the other hand, a body in totally different modifications has almost exactly the same specific heat if these foreign influences are excluded. It may, then, be said that, from our present knowledge, one and the same body may exhibit small differences with certain physical circumstances (temperature, different degree of density), but never so great that they may be taken as an explanation why a body decidedly and undoubtedly forms an exception to a regularity which might have perhaps been expected for it—provided that the determination of the specific heat, according to which the body in question forms an exception, is trustworthy, and kept free from foreign influences.

92. Among the regularities in the atomic heat of solid bodies, that found by Dulong and Petit for the elements stands foremost. A glance at the atomic heats of the so-called elements collated in § 82, shows that, for by far the greater number, the atomic heats are in fact approximately equal. But the differences in the atomic heats, even of those elements which are usually regarded as coming under Dulong and Petit's law, are often very considerable, even when the comparison is limited to those which are most easily obtained in a pure state, and even if numbers are taken for the specific heats which give the most closely agreeing atomic heats. Regnault\* sought an explana-

\* Ann. Ch. Phys. [2] lxxiii, 66, and [3] xlvi. 257.

tion of the differences of the atomic heats of the elements in the circumstance that the latter could not be investigated in comparable conditions of temperature and density ; further, that the numbers for the specific heat, as determined for solid bodies, contain, besides the true specific heat (for constant volume), also the heat of expansion. As specific heat we can indeed only take the sum of the heats necessary for heating and for expansion. But it is not yet proved that the products of the first quantity (the specific heat for constant volume) and the atomic weights would agree better than the atomic heats now do ; it is only a supposition, and even the very contrary may be possible with individual substances. Temperature has an influence on the specific heat of solid bodies, and to a different extent with different bodies. Even in this respect, also, all means are wanting by which the different temperatures at which bodies are really comparable can be known, and a comparison made of their atomic heats. The utmost possible is to determine the specific heat at such a distance from the melting point that latent heat of softening can have no influence. It is impossible to say with certainty whether the atomic heats of bodies compared at other temperatures than those which are nearly identical (ranging about  $90^{\circ}$  on each side of  $10^{\circ}$ ) will show a closer agreement. It is not probable. Changes in the specific heat of solid bodies, so long as they are unaffected by heat of softening, are small in comparison with the differences which the atomic heats of individual elements show. And it is well worth consideration that individual elements (phosphorus and sulphur, *e.g.*) at temperatures relatively near their melting points, have not materially greater specific heats than other elements (iron and platinum, for example) at temperatures relatively distant from their melting points, but, on the contrary, considerably smaller. As regards the influence of density on the specific heat, it is undoubtedly certain that the latter may somewhat vary with the former ; but it is equally so that in all cases in which substances of undoubted purity were examined and the sources of error mentioned (§ 91) excluded, this variation is too inconsiderable to give an adequate explanation of the differences of the atomic heats found for the various solid elements.

I need not here revert to the considerations developed in §§ 90 and 91, as to how far a difference in the physical condition of a solid substance exercises an essential influence on its specific heat ; for whatever view may be held with reference to this influence,

and generally with reference to the circumstances which alter the specific heat of a substance, and therewith the atomic heat, this is certain, that there are individual elements whose atomic heat is distinctly and decidedly different from that of most other elements. Such elements are, from § 82, first of all boron, carbon, and silicium.

The decision of the question whether these elements really form exceptions to Dulong and Petit's law presupposes, besides a knowledge of their specific heat, a knowledge of their atomic weight also. There can be no exceptions to Dulong and Petit's law, if, regardless of anything which may be in opposition to it, the principle is held to, that the atomic weights of the elements must be so taken as to agree with this law. As a trial whether this law is universally applicable, the atomic weights ought rather to be taken as established in another manner. It may be confessed that the determination of the true atomic weights by chemical and physico-chemical investigations and considerations is still uncertain, and many questions are still unanswered the settlement of which may influence that determination. But there seems now to be no more trustworthy basis for fixing the atomic weights of the elements than that of taking, as the atomic weights of the elements, the relatively smallest quantities which are contained in equal volumes of their gaseous or vaporous compounds, or of which the quantities contained in such volumes are multiples of the smallest numbers; and no better means appears to exist for determining the atomic weights of those elements the vapour-densities of whose compounds could not be determined, than the assumption that in isomorphous compounds the quantities of the corresponding elements are as the atomic weights of the latter. On this basis, and using this means, the numbers for the atomic weights have been determined which are contained in the last column of the Table in § 2, and are used in § 82 *et seq.* The atomic weights  $B = 10.9$ ,  $C = 12$ ,  $Si = 28$ , cannot be changed for others. That the atomic weights of tin and silicium are as 118 to 28, is further proved by the isomorphism of the double fluorides. But to these atomic weights correspond atomic heats which are far smaller than those found for most other elements. From the chemical point of view it is inadmissible to take the atomic weights of boron, carbon, and silicium\* in such a manner as to make their

\* For Regnault's observation, whether, considering the specific heat which he found for silicium, its atomic weight is to be so taken that silicic acid contains

atomic heats agree with Dulong and Petit's law. In any case these three elements form exceptions to Dulong and Petit's law. The sequel will show that this is the case with many other elements.

93. In many compounds the regularity is observed, that by dividing their atomic heat by the number of elementary atoms contained in one molecule of the compound, a quotient is obtained which comes very near the atomic heat of most of the elements—that is, 6·4. This is found in the alloys enumerated in § 82, and also in a great number of compounds of definite proportions. A few of the most important cases may be given here. For smaltine,  $\text{CoAs}_2$  (compare § 83), this quotient is  $\frac{19\cdot2}{3} = 6\cdot4$ ; for the chlorine-compounds,  $\text{RCl}$  and  $\text{RCl}^*$ , the mean of the atomic heats given in § 84 is 12·8, and the quotient  $\frac{12\cdot8}{2} = 6\cdot4$ . Of the chlorine-compounds,  $\text{RCl}_2$ , the mean atomic heat of all the determinations in § 84 is 18·5, and the quotient  $\frac{18\cdot5}{3} = 6\cdot2$ . It is also very near this value in the double chlorides; in  $\text{ZnK}_2\text{Cl}_4$  it is  $\frac{43\cdot4}{7} = 6\cdot2$ , for  $\text{R}_2\text{K}_2\text{Cl}_6$  (the mean of the determinations of  $\text{PbK}_2\text{Cl}_6$  and  $\text{SnK}_2\text{Cl}_6$ ) it is  $\frac{54\cdot8}{9} = 6\cdot1$ . For bromine-compounds,  $\text{RBr}$  (both here and in the following examples the means are taken of the determinations in § 84),  $\frac{13\cdot9}{2} = 6\cdot9$ ; for  $\text{PbBr}_2$ ,  $\frac{19\cdot6}{3} = 6\cdot5$ ; for iodine-compounds,  $\text{RI}$  and  $\text{RI}$ ,  $\frac{13\cdot4}{2} = 6\cdot7$ , and for the iodine-compounds,  $\text{RI}_2$ ,  $\frac{19\cdot4}{3} = 6\cdot5$ .

But this regularity, though met with in many compounds, is by no means universal. The oxygen-compounds of the metals correspond to it in general the less, the greater the number of oxygen-atoms they contain as compared with that of metal. The

2 atoms of silicium to 5 of oxygen, compare Ann. Chim. Phys. [3] v. Ixiii, 30. For Scheerer's remark, that according to the most probable specific heat of silicium its atomic weight must be taken so that for 1 atom of silicium there are 3 atoms of oxygen, compare Poggenдорff's Annalen, vol. cxviii, p. 182.

\* In the sequel R stands for a uni-equivalent, and  $\text{R}$  for a polyequivalent atom of a metal.

mean atomic heat of the oxides  $\text{RO}$  in § 85 is 11.1, and the quotient  $\frac{11.1}{2} = 5.6$ . The quotient for the oxides  $\text{R}_2\text{O}_3$  and  $\text{R}_2\text{O}_3$  (even excluding the determinations of alumina and boracic acid) is only  $\frac{27.2}{5} = 5.4$ ; for the oxides  $\text{RO}_2$  (even excluding the determinations for silicic acid and zircon) only  $\frac{13.7}{3} = 4.6$ ; for the oxides  $\text{RO}_3$ , the mean of Regnault's determinations only  $\frac{18.8}{4} = 4.7$ . Still smaller is the quotient for compounds which contain boron in addition to oxygen (*e.g.* for the compounds  $\text{RBO}_2$  (compare § 87) it is only  $\frac{16.8}{4} = 4.2$ ; for boracic acid,  $\text{B}_2\text{O}_3$ , it is only  $\frac{16.6}{5} = 3.3$ ); also for compounds which contain silicon in addition to oxygen (it is  $\frac{11.3}{3} = 3.8$  for silicic acid,  $\text{SiO}_2$ , compare § 85), or which contain oxygen as well as hydrogen (for ice,  $\text{H}_2\text{O}$ , it is only  $\frac{8.6}{3} = 2.9^*$ , compare § 85), or which contain hydrogen and carbon besides oxygen (*e.g.*, it is only  $\frac{36.9}{14} = 2.6$  for succinic acid,  $\text{C}_4\text{H}_6\text{O}_4$ , compare § 89). We may state in a few words which are the cases in which this quotient approximates to the atomic heat of most elements, and which the cases in which it is smaller. It is near 6.4 in those compounds which only contain elements whose atomic heats, corresponding to

\* Considering the atomic heat of liquid water to be 18, Garnier (Compt. rend. xxxv. 278) thought that the quotient obtained by dividing the atomic weight by the number of elementary atoms in one atom of the compound,  $\frac{W}{n} = 6$ , came near the atomic heat of the elements. But it requires no explanation to show that, in a comparison with the atomic heats of solid elements and solid compounds, that atomic heat must be taken for the compound  $\text{H}_2\text{O}$  which is obtained from the specific heat of ice, and not from that of water. Garnier is not alone in his error, which is rather to be ascribed to the circumstance that, formerly in considering the influence of composition or the specific heat of compounds, solid and liquid bodies were regarded as comparable in respect of their specific heat. Hermann more especially (Nouveaux Mémoires de la Société des Naturalistes de Moscou, vol iii, p. 137) compared liquid water with solid compounds, as did also Schröder (Pogg. Ann. lii, 279); so likewise did L. Gmelin, in an early discussion of this subject (Gehler's Physicalische Wörterbuch, neue Bearbeitung, vol. ix. p. 1942) while he subsequently (Handbuch der Chemie, 4 Aufl., vol. i, p. 220) more correctly compared the specific and the atomic heat of ice with that of other solid compounds.



Dulong and Petit's law, are nearly equal to 6·4; it is smaller in compounds which contain elements not coming under Dulong and Petit's law, and having a much smaller atomic heat than 6·4, and which are recognised as exceptions to this law, either directly, if their specific heat has been determined for the solid state (compare § 92), or indirectly, if it be determined in the manner to be subsequently described.

94. The determinations of specific heat given in §§ 83 to 89 contain the proofs hitherto recognised for the law that chemically-similar bodies of analogous atomic constitution have approximately the same atomic heat; and a considerable number of new examples of the prevalence of this regularity are given by my determinations. The groups of analogous compounds need not again be collated, as Neumann has done for a smaller and Regnault for a larger number of groups and for individual elements contained in them. What I will here discuss is the prevalence, beyond the limits of our previous knowledge, of the regularity, that compounds of analogous atomic constitution have approximately the same atomic heat.

To this belongs, first, the existence of this regularity in the case of chemically similar bodies, which exhibit an analogy of atomic constitution, when their formulæ are written with the atomic weights admitted in recent times for the elements, but which could not be recognized so long as the equivalents of the elements were taken as a basis, or the formula written, as by Regnault, with the use of the so-called thermal atomic weights.

The approximate equality of the atomic heats of analogous nitrates and chlorates, of the alkalis, for example, had been already observed. The same character, the haloid, is ascribed both to carbonates and to silicates; but as their formulæ were formerly written, an analogy in the composition of chlorates and nitrates, or carbonates and silicates, could not be assumed. But salts of these four different classes, as well as arseniates and metaphosphates, have analogous atomic constitutions if we assume the recent atomic weights. The same salts have then also approximately equal atomic heats. We get the atomic heat

Of chlorate of potassium, $\text{KClO}_3$ , § 88 . . . .	M* 24·8
„ the nitrates, $\text{RNO}_3$ , in § 88 . . . . .	M 23·0

\* M signifies the mean of all determinations.

Of metaphosphate of sodium, $\text{NaPO}_3$ , § 88	....	22·1
„ arseniate of potassium, $\text{KAsO}_3$ , § 88	.....	25·3
„ the carbonates, $\text{RCO}_3$ , § 86	.....	M 20·7
„ the silicates, $\text{RSiO}_3$ , § 86	.....	M 20·5

The differences in these approximately concordant atomic heats are partly essential and explainable. I shall return to this point (§ 95).

According to the more recent assumptions for the atomic weights, certain perchlorates, permanganates, and sulphates have an analogous atomic composition, and these salts have also approximately equal atomic heats; this has been found to be—

For perchlorate of potassium, $\text{KClO}_4$ , § 88	....	26·3
„ permanganate of potassium, $\text{KMnO}_4$ , § 88	..	28·3
„ the sulphates, $\text{RSO}_4$ , named in § 88	....	M 26·1

But approximate equality in the atomic heat is found, not only in such compounds of analogous chemical composition as have similar chemical character, but also in such as have totally dissimilar chemical character.

The chemical character of ferrous-ferrous oxide (magnetic iron ore) is quite different from that of neutral chromate of potassium. Ferric oxide and arsenious anhydride have a chemical character totally different from nitrates or arseniates, or bodies of similar constitution. But for the first-named and for the last-named compounds, as respectively compared with each other, there is analogy in chemical composition and approximate equality of atomic heat. The atomic heat has been found to be—

For magnetic iron ore, $\text{Fe}_3\text{O}_4$ , § 85	.....	M 37·7
„ chromate of potassium, $\text{K}_2\text{CrO}_4$ , § 87		M 36·4
„ sesquioxide of iron, $\text{Fe}_2\text{O}_3$ , § 85	.....	M 26·8
„ arsenious oxide, $\text{As}_2\text{O}_3$ , § 85	.....	.. 25·3
„ the nitrates, $\text{RNO}_3$ , named in § 88	....	.. 23·0
„ arseniate of potassium, $\text{KAsO}_3$ , § 88	.. ..	25·3

But there is even in a more extended sense approximate equality of atomic heat in bodies of analogous atomic composition. If the formulæ of the oxides,  $\text{RO}_2$  (oxide of tin for instance) are doubled, they become  $\text{R}_2\text{O}_4$ , and are then analogous to those of the sulphates,  $\text{RSO}_4$ , or of tungstate of lime or of perchlorate of

potassium and other salts. To the formulæ thus made analogous equal atomic heats correspond. The following atomic heats have been found :—

Oxide of tin, $\text{Sn}_2\text{O}_4$ , compare § 85 .....	M	27·6
Titanic oxide, $\text{Ti}_2\text{O}_4$ , „ .....	M	27·3
The sulphates, $\text{R}_2\text{SO}_4$ , in § 87 .....	M	26·1
Tungstate of calcium, $\text{CaWO}_4$ , compare § 87 .....	..	27·9
Perchlorate of potassium, $\text{KClO}_4$ , compare § 88 .....	..	26·3
Permanganate of potassium, $\text{KMnO}_4$ , compare § 88 .....	..	28·3

If the formulæ of the oxides,  $\text{RO}_2$ , are trebled, they become  $\text{R}_3\text{O}_6$ , analogous to those of the nitrates  $\text{RN}_2\text{O}_6$  (nitrate of barium, *e.g.*), and similar salts. Here also approximately equal atomic heats correspond to the formulæ thus made analogous. The atomic heats are as follows :—

Oxide of tin, $\text{Sn}_3\text{O}_6$ , compare § 85 .....	M	41·4
Titanic oxide, $\text{Ti}_3\text{O}_6$ , „ .....	M	41·0
The nitrates, $\text{RN}_2\text{O}_6$ , in § 88 .....	M	38·1
Metaphosphate of calcium, $\text{CaP}_2\text{O}_6$ , compare § 88 ..	..	39·4

How little the atomic heat of compounds depends on their chemical character may be proved from a more extended series of examples than those adduced in the preceding. It is, however, unnecessary to dwell upon this. The comparisons and considerations contained in the sequel complete what has here been developed as a proof of the principle that the atomic heat of bodies is independent of their chemical character.

95. The foregoing comparisons give examples of cases in which bodies of analogous atomic structure, with a totally different chemical character, have approximately the same atomic heat; they show that with reference to the atomic heat, uni-equivalent and multi-equivalent elementary atoms have the same influence, which, indeed, followed already from Regnault's comparisons; that the atomic heat of a substance for its multifold atomic formula may be compared with that of another substance for a simple atomic formula. The preceding contains a generalization of Neumann's law; but as certainly as this law is recognised in the preceding in a more general manner than was formerly assumed, as little is it universally applicable.

Regnault's investigations have shown that Neumann's law is

not rigidly valid. Even for those compounds which contain the same element as electronegative constituent, and have similar atomic constitution, he found the atomic heats as much as  $\frac{1}{10}$  to  $\frac{1}{5}$  different from each other.\* The reason of this he seeks in the same circumstances, which in his view prevent a closer agreement in the atomic weights of the elements (compare § 92).

Differences of this kind, and even of greater amount, occur in the atomic heats of compounds for which closer agreement in these numbers might be expected—of such compounds, that is, as contain elements of the same, or nearly the same atomic heat combined with the same other element in the same atomic proportion. To this belongs the fact that the atomic heat has been found so different (§ 85) for the isomorphous compounds, magnetic iron ore (37·7), chrome iron ore (31·2), and spinelle (27·7), and for alumina (21·3) and for sesquioxide of iron (26·8). In the atomic heats of such analogous compounds there are differences for which, or rather for the magnitude of which, as furnished by our present observations, I know at present no adequate explanation.

But there is another kind of difference in the atomic heats of analogous compounds, which exhibits a regularity, and for which an explanation can be given. Certain elements impress on all their compounds the common characteristic, that their atomic heat is much smaller than that of most analogous compounds. The atomic heat of boracic anhydride,  $B_2O_3$ , is only 16·6, while that of most other compounds,  $R_2O_3$  and  $\bar{R}_2O_3$ , is between 25 and 28 (§ 85). The atomic heat of the borates  $R B O_2$ , is (§ 87) only 16·8, while that of  $\bar{R}_2O_2$ , as the mean of the determination in § 85, is 22·2. The atomic heat of  $PbB_2O_4$  is (§ 87) only 26·5, while that of  $Fe_3O_4$  (§ 85) in the mean is 37·7. Similar results have been obtained for compounds of certain other elements, of carbon and of silicum, for instance, that is, of those elements which in the free state have a smaller atomic heat than that of most other elements.

This observation leads to the question whether the elements enter into compounds with the atomic heats which they have in the free state, and in connexion with this, how far is it permissible to make an indirect determination of the atomic heat of the elements (in their solid state) from the atomic heats of their (solid) compounds.

\* Ann. Ch. Phys. [3], i, 196.

96. The assumption that elements enter into compounds with the atomic heats they have in the free state would be inadmissible, if not only the atomic structure as expressed by the empirical formula, but also the grouping of the elements to proximate constituents, as is endeavoured to be expressed by the rational formula, influenced the atomic heat of the compounds. That the latter is not the case is very probable from the comparisons made in § 94, where approximately equal atomic heats were obtained for compounds of analogous empirical formulæ, even with the greatest dissimilarity of chemical character. That that, which may be supposed and expressed by the so-called rational formula in reference to the internal constitution of compounds, does not affect the atomic heat, becomes more probable from the fact that chemically similar, and even isomorphous compounds, one of which contains an atomic group in the place of an individual atom in the other, exhibit dissimilar atomic heats. This is seen, for instance, in comparing analogous chlorine and cyanogen compounds ( $Cy=CN$ ) the latter have far greater atomic heats. Thus the atomic heat

Of chloride of mercury, $HgCl_2$ , § 84, is .....	18·0
„ cyanide of mercury, $HgCy_2$ , § 89 .....	25·2
„ chloride of zinc and potassium, $ZnK_2Cl_4$ , § 84 ....	43·4
„ cyanide of zinc and potassium, $ZnK_2Cy_4$ , § 89 ....	59·6

In like manner ammonium-compounds ( $Am=NH_4$ ) have atomic heats considerably greater than the corresponding potassium-compounds. This is seen from the following Table:—

Chloride of potassium, $KCl$ , § 84 .....	M	12·9
„ ammonium, $AmCl$ , § 84 .....		20·0
Nitrate of potassium, $KNO_3$ , § 88 .....	M	23·5
„ ammonium, $AmNO_3$ , § 88 .....		36·4
Sulphate of potassium $K_2SO_4$ , § 87 .....	M	33·6
„ ammonium, $Am_2SO_4$ , § 87 .....		46·2

97. That undecomposable atoms and atomic groups are contained in compounds with the atomic heats they have in the free state, is further probable from the fact that the sum of the atomic heats of such atoms, or atomic groups, as when united form a certain compound, is equal or approximately equal to the atomic heat of this compound. For many compounds whose elements obey Dulong and

Petit's law, what has been stated in § 93 contains the proof that the atomic heat of these compounds is equal to the sum of the atomic heats of the elementary atoms contained in one atom of the compounds. That this is also observed when atomic groups are supposed to be united, forming more complicated compounds, will be seen by bringing forward a few examples. The atomic heat has been found—

For the oxides, $\text{R}_2\text{O}$ , enumerated in § 85	.....	M	11.1
„ sesquioxide of iron, $\text{Fe}_2\text{O}_3$ , § 85	.....	M	26.8
			37.9
Sum for $\text{FeRO}_4$	.....		37.9
„ magnetic iron ore, $\text{Fe}_3\text{O}_4$ , § 85	.....	M	37.7
„ the oxides, $\text{R}_2\text{O}$ , in § 85	.....	M	11.1
„ the acids, $\text{R}_2\text{O}_3$ , in 85, according to Regnault		M	18.8
			29.9
Sum for $\text{RRO}_4$	.....		29.9
„ chromate of lead, $\text{PbCrO}_4$ , § 87	.....		29.0
„ the oxides named in § 85, $\text{RO}$	.....	M	11.1
„ binoxide of tin, $\text{SnO}_2$ , § 85	.....	M	18.8
			24.9
Sum for $\text{RRO}_3$	.....		24.9
„ sesquioxide of iron, $\text{Fe}_2\text{O}_3$ , § 85	.....	M	26.8
„ chromate of potassium, $\text{K}_2\text{CrO}_4$ , § 87	.....	M	36.4
„ the anhydrides $\text{R}_2\text{O}_3$ , in § 85 (Regnault)	.....		18.8
			55.2
Sum for $\text{K}_2\text{CrRO}_7$	....		55.2
„ acid chromate of potassium, $\text{K}_2\text{Cr}_2\text{O}_7$ , § 87	..	M	53.3
„ binoxide of tin, $\text{Sn}_3\text{O}_6$ , § 85	.....	M	41.4
„ base, $\text{R}_2\text{O}_2$ , mean of determinations, § 85	..	M	22.2
			63.6
Sum for $\text{R}_5\text{O}_8$	.....		63.6
„ arseniate of lead, $\text{Pb}_3\text{As}_2\text{O}_8$ , § 88	.....		65.4

To this belongs the fact that water is contained in solid compounds with the atomic heat of ice.\* The different determinations of the specific heat of this substance (§ 85) gave the atomic

\* Even before Person (compare § 14) L. Gmelin had speculated (*Handbuch der Chemie*, [4] Aufl. vol. i, p. 223) whether from the atomic heats of anhydrous sulphate of calcium and of ice that of gypsum could be calculated. The results of calculation deviated considerably from the atomic heat as deduced from the observed specific heat of gypsum; the specific heat, and therewith the atomic heat of ice, were not at that time correctly known.

heat for greater distances from  $0^{\circ}$ , 8.6, and for temperatures nearer  $0^{\circ}$ , 9.1 to 9.2. The atomic heats have been found—

		For $H_2O$ .
For $BaCl_2 \cdot 2H_2O$ , § 84	41.7	
„ the chlorides, $R Cl_2$ , § 84	M 18.5	
	Remains for $2H_2O$	11.6
„ $CaCl_2 \cdot 6H_2O$ , § 84	75.6	
„ the chlorides, $R Cl_2$ , § 84	M 18.5	
	Remains for $6H_2O$	9.5
„ Brucite, $MgO \cdot H_2O$ , § 85	18.1	
„ the oxides, $RO$ , § 85	M 11.1	
	Remains for $H_2O$	7.0
„ diopside, $CuSiO_3 \cdot H_2O$ , § 86	28.7	
„ the silicates, $RSiO_3$ , § 86	M 20.5	
	Remains for $H_2O$	8.2
„ $Na_2B_4O_7 \cdot 10H_2O$ , § 87	146.9	
„ $Na_2B_4O_7$ , § 87	47.1	
	Remains for 10 $H_2O$	10.0
„ gypsum, $CaSO_4 \cdot 2H_2O$ , § 87	M 45.8	
„ the sulphates, $RSO_4$ , § 87	M 26.1	
	Remains for $2H_2O$	9.9

The Tables in §§ 84 to 89 contain data for several such comparisons, which lead to the same result as the preceding—that the atomic heat of water contained in solid compounds may, by subtracting the atomic heat of the anhydrous solid from that of the hydrated solid compound, be obtained in sufficient approximation to the atomic heat deduced from the direct determination of the specific heat of ice. The deviations from each other and from the atomic heat of ice as directly determined, which these indirect determinations exhibit, are not to be wondered at, when it is considered that all uncertainties in the atomic heats, from whose difference the atomic heat of solid water is deduced, are concentrated upon this difference.

98. The view already expressed and defended (compare especially §§ 12 and 13), that atoms and atomic groups are contained

in solid compounds with the same atomic heat that they have in the free state, is opposed to the view which has also been frequently expressed and defended—that the atomic heat of an element may in certain compounds differ from what it is in the free state, and may be different in different compounds. This view, and the reasons which may possibly be urged in its favour, must here be discussed.

The first statement of this view (compare § 6) simply goes to assert that the atomic heats of compounds may be calculated in accordance with the values resulting from the determinations of the specific heat, assuming that one constituent of the compound has the same atomic heat as in the free state, the other an altered one. What alteration is to be assumed depends merely on what assumption adequately satisfies the observed specific heat of the compound. The accuracy of the assumption is susceptible of no further control; the assumption itself cannot be regarded as an explanation of the observed atomic heat of the compound. And nothing is altered in this by assuming (compare §§ 6 and 11) that the changes in the atomic heat of a substance on entering into chemical compounds take place in more or less simple ratios.

A greater degree of probability must be granted to the view (compare § 10) that the atomic heats of the constituents of compounds, and the differences in the atomic heats of these bodies, according as they are combined or in the free state, depend upon the state of condensation in which these bodies are contained. If, for instance, from a consideration of the specific gravities or specific volumes (the quotient of the specific weights into the atomic weights) of compounds and of their constituents, a conclusion could be drawn with some degree of certainty as to the state of condensation in which the latter are present in the former, and if definite rules could be given for the variations of the atomic heats with the state of condensation, the result of such an investigation, if it agreed with the observed results for the atomic heats of compounds, might be called an explanation of these observations. But what is here presupposed is partially not attained and partially not attempted. And, moreover, as far as can be judged from individual cases, the same element, when present in different states of condensation, appears to have the same atomic heat. It has been attempted to deduce the state of condensation, or the specific volume, of oxygen in its compounds with heavy metals, by subtracting from the specific volume of the oxide



that of the metal in it, and considering the remainder as the volume of oxygen. It would follow from this that the specific volume of oxygen in cuprous oxide is much greater (about four times as great) than in stannic oxide. But if the atomic heat of oxygen be deduced by subtracting from the atomic heat of the oxide that of the metal in it, it is found that the atomic heat of oxygen in cuprous oxide and in stannic oxide gives almost exactly the same number. Hence it does not seem that the state of condensation in which a constituent may be contained in a compound has any material influence on the atomic heat of this constituent.

99. From all that has been said in the foregoing paragraphs the following must be adhered to. (1) Each element in the solid state, and at a sufficient distance from its melting point, has *one* specific or atomic heat, which may indeed vary to a certain extent with physical conditions, different temperature, or density, for instance, but not so considerably as to be regarded in considering in what relations the specific heat stands to the atomic weight or composition; and (2) that each element has essentially the same specific or atomic heat in compounds as it has in the free state. On the basis of these two fundamental laws we may now investigate what atomic heats individual elements have in the solid free state and in compounds. According to these propositions, indirect deductions of the atomic heats of such elements as could not be investigated in the solid free state are admissible in this sense; that from the atomic heat of a compound containing such an element the atomic heat of everything else in the compound is subtracted, and the remainder considered as the expression for the atomic heat of that element. Such indirect determinations of the atomic heat of elements may be uncertain, partly because the atomic heat of the compounds is frequently not known with certainty, as is seen from the circumstance that analogous compounds, for which there is every reason to expect the same atomic heat, are found by experiment to have atomic heats not at all agreeing; but more especially because the entire relative uncertainty in the atomic heats for a compound, and for that which is to be subtracted from its composition, is concentrated upon a small number, the residue remaining in the deduction. But when such deductions are made, not merely for individual cases, but for different compounds, and for entire series of corresponding compounds, they may be considered sufficiently

trustworthy to make the speculations based upon them worthy of attention. Of course in indirectly deducing the atomic heat of an element, its simpler compounds, and those containing it in greatest quantity (measured by the number of atoms), promise the most trustworthy results.

100. For *silver, aluminium, arsenic, gold, bismuth, bromine, cadmium, cobalt, copper, iron, mercury, iodine, iridium, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, osmium, lead, palladium, platinum, rhodium, antimony, selenium, tin, tellurium, thallium, tungsten, and zinc*, it may be assumed, from the determinations of their specific heat in the solid state (§ 82), that their atomic heats, in accordance with Dulong and Petit's law, are approximately equal, the average being 6·4. I do not believe that all these elements have really the same atomic heat, but think that some of them will hereafter be considered as exceptions to the above-mentioned law, as it will in the sequel be proved that several other elements have an atomic heat differing from 6·4. But for none of the previously mentioned elements are the present data, and the presumed deviation of the atomic heat from that of other elements, sufficient to justify their separation from them.

With the elements just mentioned *chlorine* must be associated from the close agreement of the corresponding chlorine, bromine, and iodine compounds (§ 84), and of the compounds  $\text{KClO}_3$ , 24·8, and  $\text{KAsO}_3$ , 25·3 (§ 88). To the atomic heats of these latter compounds those of individual salts,  $\text{KNO}_3$ , approximate closely; the latter gave (§ 88) 21·8–24·4, mean 23·0, which, on the whole, agrees nearly enough with those found for the metallic oxides,  $\text{R}_2\text{O}_3$  (§ 85). I count *nitrogen* also among the elements whose atomic heat may be assumed at 6·4, like that of most other elements, without, however, considering the determination of the atomic heat of this element as very trustworthy. To deduce the atomic heat of this element with certainty, compounds are wanting which contain, besides nitrogen, elements whose atomic heat has been directly determined. The fact that the atomic heat of the nitrates,  $\text{R}_2\text{N}_2\text{O}_6$ , was found (§ 88) in the mean to be 38·1, a third of which, 12·7, is somewhat less than the average atomic heat found for the oxides of heavy metals of the formula  $\text{RO}_2$ , might be a reason for assigning to nitrogen a smaller atomic heat; while, on the other hand, the atomic heats of other nitrogen-compounds, in which, it is true, other elements

enter whose atomic heat is only indirectly determined, do not favour this view.

In the class of elements with the atomic heat about 6·4, *barium*, *calcium*, and *strontium* may be placed, from the agreement in the atomic heats of their compounds with the atomic heats of corresponding compounds of such elements as have been found by the direct determination of their specific heat in the free solid state to belong to that class (compare the atomic heats of the compounds  $\text{RCl}_2$  in § 84,  $\text{RCO}_3$  in § 86,  $\text{RSO}_4$  in § 87, and  $\text{RN}_2\text{O}_6$  in § 88); further, *rubidium* (compare the atomic heats of the compounds  $\text{RCl}$  in § 84, and  $\text{R}_2\text{CO}_3$  in § 86); then also *chromium* (from the agreement in the atomic heats of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , § 84), and *titanium* (from the agreement in the atomic heats of  $\text{TiO}_2$  and  $\text{SrO}_2$ , § 84). To place *zirconium* in the same class has no other justification than that, on this assumption, the atomic heat of zircon may be calculated in accordance with that deduced from the observed specific heat of this mineral.

101. According to direct determinations of the specific heat, *sulphur* and *phosphorus* do not belong to this class. The more trustworthy determinations (for the sulphur the last two, for phosphorus the last three of the numbers in § 82) assign to these elements the atomic heat 5·4. That sulphur has a smaller atomic heat than the elements discussed in the last paragraphs, follows from the atomic heats of sulphur-compounds, compared with those of the corresponding compounds of such elements as have an atomic heat = 6·4. The average atomic heat of compounds  $\text{RS}$  and  $\text{R}_2\text{S}$  is 11·9, according to the determinations in § 83, while those of chlorine-compounds  $\text{RCl}$  and  $\text{R}_2\text{Cl}$  (§ 84) = 12·8, that of the corresponding bromine-compounds = 13·9, and of the corresponding iodine-compounds = 13·4. In comparing more complicated sulphur-compounds, sulphates, for instance, with other compounds of analogous composition, the same is met with, although such complicated compounds are of little value in giving data for deciding on such small differences. The specific heat of the simpler phosphorus-compounds has not been investigated; for more complicated compounds, although they point to a smaller atomic heat for P than 6·4, the above remark also applies.

The determinations of the specific heat of *silicium* give for this element also a smaller atomic heat than 6·4 (compare § 82), and the same conclusion results from a comparison of the atomic heats of  $\text{SiO}_2$ , and the oxides,  $\text{RO}_2$ , of the silicates  $\text{RSiO}_3$ , and

the oxides  $R_2O_3$ . The atomic heat to be assigned to silicium cannot as yet be settled with any degree of certainty. Direct determinations, varying considerably from each other, give a specific heat mostly greater than 4; while the numbers obtained indirectly, and themselves also not closely agreeing, are partly considerably smaller. If in the sequel, I put the atomic heat of silicium at 3·8, corresponding to the lowest number found for the specific heat of this element, I do so for want of other and more certain data. I consider this number as quite uncertain.

The atomic heat of *boron*, from the direct determinations of the specific heat, is considerably smaller than 6·4; and the atomic heats of boron-compounds confirm this conclusion, as was discussed in §§ 93 and 95. By comparing the atomic heats of such boron and sulphur-compounds as contain, along with boron and sulphur, the same elements in the same proportions, the atomic heat of boron is found to be half that of sulphur. The atomic heat of  $KBO_2 = 16·8$  is exactly half that found for  $K_2SO_4 = 33·6$ ; the atomic heat of  $PbB_2O_4 = 26·5$  is almost exactly equal to that for  $PbSO_4 = 25·7$ . Taking the atomic heat of S, in accordance with the above discussion, at 5·4, that of B would be 2·7; the numbers obtained directly for the atomic heat of boron (§ 82) from the experiments on the specific heat of this element agree with sufficient accuracy. In the sequel I take the atomic heat of boron at 2·7. A smaller number is obtained in other comparisons; for instance, of the atomic heats of  $B_2O_3$  and of the oxides  $R_2O_3$ , or of the salts  $RBO_2$  and the oxides  $R_2O_2$ ; but in such indirect determinations of the atomic heat, where such small numbers are to be determined, as is here the case with the atomic heat of boron, the results are very uncertain, owing to the fact that the entire uncertainty in the atomic heats of the compounds, and in the assumption that the elements corresponding to boron in compounds of analogous composition have really the atomic heat = 6·4, is thrown on the final result.

Lastly, *carbon* also, from the direct determinations of its specific heat (§ 82), has a much smaller atomic heat than 6·4. The same result follows from a comparison of the atomic heats of carbon-compounds: the atomic heat of the carbonates,  $R_2CO_3 = 28·4$  as the mean of the determinations in § 86, is much smaller than that of  $R_2O_3 (= 3RO)$ , which is the mean of the numbers in § 85 = 33·3; the atomic heat of the carbonates  $R_2CO_3 = 20·7$ , as the mean of the determinations in § 86, is much smaller than

27·1, the number found for  $\text{As}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$  as the atomic heat of oxides  $\text{R}_2\text{O}_3$ . I put the atomic heat of carbon at 1·8 for C, as deduced from the determination of the specific heat of its purest variety, diamond.

102. In the preceding paragraphs I have discussed the elements which, from the determinations of their specific heat in the solid free state, have a smaller atomic heat than about 6·4. There remain to be discussed a few elements whose atomic heats are also less than those of most other elements, but can only be deduced from those of their compounds.

To this category belong *hydrogen*\*, even if the indirect determination of its atomic heat in the solid state is liable to the uncertainty just discussed. The atomic heat of water,  $\text{H}_2\text{O}$ , is (§ 85) = 8·6, and smaller by 7 than that of suboxide of copper,  $\text{Cu}_2\text{O}$ , which was found in the mean to be 15·6; the atomic heat of hydrogen would thus be  $\frac{1}{2}$  = 3·5 less than that of the elements to which copper belongs, as regards its atomic heat; hence the former would be 6·4 - 3·5 = 2·9. The atomic heat of chloride of ammonium,  $\text{NH}_4\text{Cl}$ , has been found to be 20·0 (§ 84); the subtraction of the atomic heats for N + Cl = 6·4 + 6·4 = 12·8, leaves 7·2 as the atomic heat of 4H, and therefore 1·7 for that of H. The atomic heat of nitrate of ammonia,  $\text{N}_2\text{H}_4\text{O}_3$ , is 36·4 (§ 88); subtracting therefrom as the atomic heat of  $\text{N}_2 + \text{O}_3$ , the number 27·1, which has previously been frequently mentioned as the atomic heat of oxides  $\text{R}_2\text{O}_3$ , we have 9·3 as the atomic heat of 4H, that is 2·3 for that of H. I put in the sequel the atomic heat of *hydrogen* at 2·3.

That *oxygen* has a smaller atomic heat than 6·4, follows from the fact that the oxygen compounds of the metals have a considerably smaller atomic heat than the corresponding chlorides, iodides, or bromides. For instance, the atomic heat of the oxides  $\text{RO}$  is as the mean of the determinations in § 85 = 11·1, while that of the chlorides  $\text{RCl}$  and  $\text{RCl}$  (§ 84), is 12·8, that of the corresponding bromides 13·9, and of the corresponding iodides 13·4. That of the oxides,  $\text{RO}_2$ , as the mean of the determinations in § 85, of  $\text{MnO}_2$ ,  $\text{SnO}_2$ , and  $\text{TiO}_2$  is 13·7, while that of

\* L. Gmelin (Handbuch der Chemie, 4 Aufl., vol. i, pp. 216 and 222) ascribed to hydrogen the same capacity for heat as that of an equivalent quantity of lead or mercury (H = 1, Cu = 31·7, Hg = 100); Schröder (Pogg. Ann. vol. lvii. p. 279) and Cannizzaro (Il Nuovo Cimento, vol. vii. p. 342) ascribed to hydrogen the same atomic heat as that of most other elements (H = 1, Cl = 35·5, Cu = 63·4, Hg = 200).

the chlorides  $\mathbb{R}\text{Cl}_2$  (§ 85) is 18.5, and of the iodides  $\mathbb{R}\text{I}_2 = 19.4$ . Taking the atomic heat of the other elements, which are contained in the following compounds, at 6.4, the atomic heat of oxygen, as deduced from the atomic heat of the oxides  $\mathbb{R}\text{O}$  (11.1 in the mean), is = 4.7; as deduced from the oxides  $\mathbb{R}_2\text{O}_3$  (27.1 as the mean of the oxides of this formula previously frequently mentioned), it is = 4.8; from the above oxides,  $\mathbb{R}\text{O}_2$  (13.7 in the mean), it is = 3.7; it is found (compare § 88) from  $\text{KAsO}$  (25.3) to be 4.1; from  $\text{Pb}_3\text{As}_2\text{O}_8$  (65.4) to be 4.2; from  $\text{KClO}_3$  (24.8) to be 4.0; from  $\text{KClO}_4$  (26.3) to be 3.4; from  $\text{KMnO}_4$  (28.3) to be 3.9. In the sequel the round number 4 is taken for the atomic heat of O.

*Fluorine* appears, lastly, to have an atomic heat considerably smaller than 6.4. The atomic heat of fluoride of calcium,  $\text{CaFl}_2$ , has been found to be (§ 84) only 16.4, considerably smaller than the corresponding chlorides, bromides, and iodides. I put the atomic heat of fluorine at  $\frac{16.4-6.4}{2} = 5$ .

103. Taking, in accordance with what has just been said, the atomic heat which an element has in a solid compound,

At 6.4 for Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, I, Ir, K, Li, Mg, Mn, Mo, N, Na, Ni, Os, Pb, Pd, Pt, Rb, Rh, Sb, Se, Sn, Sr, Te, Ti, Tl, W, Zn, and Zr,

At 5.4 for S and P, at 5 for Fl, 4 for O, 3.8 for Si, 2.7 for B, 2.3 for H, and 1.8 for C; and assuming that the atomic heat of a solid is given by the sum of the atomic heats of the elements in it, we obtain the atomic heats; and dividing them by the atomic weights, we obtain the specific heats, in sufficiently close agreement with the specific heats as obtained by direct determinations of this property.

In the following Table, I give for all compounds for which the specific heat has been determined in a trustworthy manner, the specific heat calculated on these assumptions, compared with the numbers found experimentally. This calculation and this comparison are given in the same order which was followed in the synopsis § 82 to 89, and I refer to the latter as regards special remarks on the determinations. To distinguish the observers, N. again stands for Neumann, R. Regnault, Kp. Kopp, Pr. Person, A. Alluard, and Pp. Pape.

*Alloys.* (Compare § 82.)

	Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.	
Bi Sn .. ..	328	12·8	0·0390	0·0400	R.
Bi Sn <sub>3</sub> .. ..	446	19·2	0·0430	0·0450	R.
Bi Sn <sub>2</sub> Sb .. ..	568	25·6	0·0451	0·0462	R.
Bi Sn <sub>2</sub> Sb Zn <sub>3</sub> .. ..	698·4	38·4	0·0550	0·0566	R.
Pb Sb .. ..	329	12·8	0·0389	0·0388	R.
Pb Sn .. ..	325	12·8	0·0394	0·0407	R.
Pb Sn <sub>2</sub> .. ..	443	19·2	0·0433	0·0451	R.

104. *Arsenides and Sulphides.* (Compare § 83.)

Co As <sub>2</sub> .. ..	208·8	19·2	0·0919	0·0920	N.		
Ag <sub>2</sub> S .. ..	248	18·2	0·0784	0·0746	R.		
Co As S .. ..	166	18·2	0·110	0·107	N.		
Cu <sub>2</sub> S .. ..	158·8	18·2	0·115	0·121	R.	0·120	Kp.
Fe As S .. ..	163	18·2	0·112	0·101	N.		
As S .. ..	107	11·8	0·110	0·111	N.		
Co S .. ..	90·8	11·8	0·130	0·125	R.		
Cu <sub>2</sub> Fe <sub>1</sub> S .. ..	91·7	11·8	0·129	0·129	N.	0·131	Kp.
Fe S .. ..	88	11·8	0·134	0·136	R.		
Hg S .. ..	232	11·8	0·0509	0·052	N.	0·0512	R. 0·0517 Kp.
Ni S .. ..	90·8	11·8	0·130	0·128	R.		
Pb S .. ..	239	11·8	0·0494	0·053	N.	0·0509	R. 0·0490 Kp.
Sn S .. ..	150	11·8	0·0783	0·0837	R.		
Zn S .. ..	97·2	11·8	0·121	0·115	N.	0·123	R. 0·120 Kp.
Fe <sub>7</sub> S <sub>8</sub> .. ..	648	88·0	0·136	0·153	N.	0·160	R.
As <sub>2</sub> S <sub>2</sub> .. ..	246	29·0	0·118	0·113	N.		
Bi <sub>2</sub> S <sub>3</sub> .. ..	516	29·0	0·0662	0·060	R.		
Sb <sub>2</sub> S <sub>3</sub> .. ..	340	29·0	0·0853	0·0907	N.	0·0840	R.
Fe S <sub>2</sub> .. ..	120	17·2	0·143	0·128-0·133	N.	0·130	R. 0·126 Kp.
Mo S <sub>2</sub> .. ..	160	17·2	0·107	0·107	N.	0·123	R.
Sn S <sub>2</sub> .. ..	182	17·2	0·0945	0·119	R.		

105. *Chlorides, Bromides, Iodides, and Fluorides.* (Compare § 84.)

Ag Cl .. ..	143·5	12·8	0·0892	0·0911	R.		
Cu Cl .. ..	98·9	12·8	0·129	0·138	R.		
Hg Cl .. ..	235·5	12·8	0·0543	0·0521	R.		
K Cl .. ..	74·6	12·8	0·172	0·173	R.	0·171	Kp.
Li Cl .. ..	42·5	12·8	0·301	0·282	R.		
Na Cl .. ..	58·5	12·8	0·219	0·214	R.	0·213-0·219	Kp.
Rb Cl .. ..	120·9	12·8	0·106	0·112	Kp.		
N H <sub>4</sub> Cl .. ..	53·5	22·0	0·411	0·373	Kp.		
Ba Cl <sub>2</sub> .. ..	208	19·2	0·0923	0·0896	R.	0·0902	Kp.
Ca Cl <sub>2</sub> .. ..	111	19·2	0·173	0·164	R.		
Hg Cl <sub>2</sub> .. ..	271	19·2	0·0708	0·0689	R.	0·640	Kp.
Mg Cl <sub>2</sub> .. ..	95	19·2	0·202	0·195	R.	0·191	Kp.
Mn Cl <sub>2</sub> .. ..	126	19·2	0·152	0·143	R.		
Pb Cl <sub>2</sub> .. ..	278	19·2	0·0691	0·0664	R.		
Sn Cl <sub>2</sub> .. ..	189	19·2	0·102	0·102	R.		
Sr Cl <sub>2</sub> .. ..	158·6	19·2	0·121	0·120	R.		
Zn Cl <sub>2</sub> .. ..	136·2	19·2	0·141	0·136	R.		
Ba Cl <sub>2</sub> · 2H <sub>2</sub> O .. ..	244	36·4	0·149	0·171	Kp.		

	Atomic weight.	Atomic heat.	Calculated.	Specific heat.	Calculated.	Specific heat.	Observed.				
Ca Cl <sub>2</sub> . 6H <sub>2</sub> O ..	219	70.8	0.323	0.345	Pr.						
Zn K <sub>2</sub> Cl <sub>4</sub> ..	285.4	44.8	0.157	0.152	Kp.						
Pt K <sub>2</sub> Cl <sub>6</sub> ..	488.6	57.6	0.118	0.113	Kp.						
Sn K <sub>2</sub> Cl <sub>6</sub> ..	409.2	57.6	0.141	0.133	Kp.						
Cr <sub>2</sub> Cl <sub>6</sub> ..	317.4	51.2	0.161	0.143	Kp.						
Ag Br ..	188	12.8	0.0681	0.0739	R.						
K Br ..	119.1	12.8	0.107	0.113	R.						
Na Br ..	103	12.8	0.124	0.138	R.						
Pb Br <sub>2</sub> ..	367	19.2	0.0523	0.0533	R.						
Ag I ..	235	12.8	0.0545	0.0616	R.						
Cu I ..	190.4	12.8	0.0672	0.0687	R.						
Hg I ..	327	12.8	0.0391	0.0395	R.						
K I ..	166.1	12.8	0.0771	0.0819	R.						
Na I ..	150	12.8	0.0853	0.0868	R.						
Hg I <sub>2</sub> ..	454	19.2	0.0423	0.0420	R.						
Pb I <sub>2</sub> ..	461	19.2	0.0416	0.0247	R.						
Ca Fl <sub>2</sub> ..	78	16.4	0.210	0.208	N.	0.215	R.	0.209	Kp.		
Al Na <sub>3</sub> Fl <sub>6</sub> ..	210.4	55.6	0.264	0.238	Kp.						

## 106. Oxides. (Compare § 85.)

Cu <sub>2</sub> O ..	142.8	16.8	0.118	0.107	N.	0.111	Kp.				
H <sub>2</sub> O ..	18	8.6	0.478	0.480	Pr.	0.474	R.				
Cu O ..	79.4	10.4	0.131	0.137	N.	0.142	R.	0.123	Kp.		
Hg O ..	216	10.4	0.0481	0.049	N.	0.052	R.	0.053	Kp.		
Mg O ..	40	10.4	0.260	0.276	N.	0.244	R.				
Mn O ..	71	10.4	0.146	0.157	R.						
Ni O ..	74.8	10.4	0.139	0.159	R.						
Pb O ..	22.3	10.4	0.0466	0.0512	R.	0.0553	Kp.				
Zn O ..	81.2	10.4	0.128	0.132	N.	0.125	R.				
Mg O . H <sub>2</sub> O ..	58	19.0	0.328	0.312	Kp.						
Fe <sub>3</sub> O <sub>4</sub> ..	232	35.2	0.152	0.164	N.	0.168	R.	0.156	Kp.		
Mg Al <sub>2</sub> O <sub>5</sub> ..	142.8	35.2	0.246	0.194	Kp.						
Mg $\frac{1}{2}$ Fe $\frac{1}{2}$ Cr $\frac{3}{2}$ Al $\frac{1}{2}$ O <sub>4</sub> ..	196	35.2	0.179	0.159	Kp.						
Al <sub>2</sub> O <sub>3</sub> ..	102.8	24.8	0.241	0.197	N.	0.217	R.				
As <sub>2</sub> O <sub>3</sub> ..	198	24.8	0.125	0.128	R.						
B <sub>2</sub> O <sub>3</sub> ..	69.8	17.4	0.249	0.237	R.						
Bi <sub>2</sub> O <sub>3</sub> ..	468	24.8	0.0530	0.0605	R.						
Cr <sub>2</sub> O <sub>3</sub> ..	152.4	24.8	0.163	0.196	N.	0.180	R.	0.177	Kp.		
Fe <sub>2</sub> O <sub>3</sub> ..	160	24.8	0.155	0.169	N.	0.167	R.	0.154	Kp.		
Fe $\frac{3}{4}$ Ti $\frac{1}{4}$ O <sub>3</sub> ..	155.5	24.8	0.160	0.176	N.	0.177	Kp.				
Sb <sub>2</sub> O <sub>3</sub> ..	292	24.8	0.0849	0.0901	R.						
Mn <sub>2</sub> O <sub>3</sub> . H <sub>2</sub> O ..	176	33.4	0.189	0.176	Kp.						
Mn O <sub>2</sub> ..	87	14.4	0.166	0.159	Kp.						
Si O <sub>2</sub> ..	60	11.8	0.197	0.188	N.	0.191	R.	0.186	Kp.		
Si $\frac{1}{2}$ Zr $\frac{1}{2}$ O <sub>2</sub> ..	90.8	13.1	0.144	0.146	R.	0.132	Kp.				
Sn O <sub>2</sub> ..	150	14.4	0.096	0.093	N.	0.093	R.	0.089	Kp.		
Ti O <sub>2</sub> ..	82	14.4	0.176	0.172	N.	0.171	R.	0.159	Kp.		
Mo O <sub>2</sub> ..	144	18.4	0.128	0.132	R.	0.154?	Kp.				
W O <sub>3</sub> ..	232	18.4	0.0793	0.0798	R.	0.0894?	Kp.				

## 107. Carbonates and Silicates. (Compare § 86.)

K <sub>2</sub> C O <sub>3</sub> ..	138.2	26.6	0.192	0.216	R.	0.206	Kp.				
Na <sub>2</sub> C O <sub>3</sub> ..	106	26.6	0.251	0.273	R.	0.246	Kp.				



	Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.					
Rb <sub>2</sub> C O <sub>3</sub> .. ..	230.8	26.6	0.115	0.123	Kp.				
Ba C O <sub>3</sub> .. ..	197	20.2	0.103	0.108	N.	0.110	R.		
Ca C O <sub>3</sub> .. ..	100	20.2	0.202	0.203	N.	0.209	R.	0.205	Kp.
Ca $\frac{1}{2}$ Mg $\frac{1}{2}$ C O <sub>3</sub> .. ..	92	20.2	0.220	0.216	N.	0.218	R.	0.206	Kp.
Fe $\frac{2}{3}$ Mn $\frac{1}{3}$ Mg $\frac{1}{3}$ C O <sub>3</sub> .. ..	112.9	20.2	0.179	0.166	Kp.				
Mg $\frac{2}{3}$ Fe $\frac{1}{3}$ C O <sub>3</sub> .. ..	91.1	20.2	0.222	0.227	N.				
Pb C O <sub>3</sub> .. ..	267	20.2	0.0757	0.0814	N.	0.0791	Kp.		
Sr C O <sub>3</sub> .. ..	147.6	20.2	0.137	0.145	N.	0.145	R.		
Ca Si O <sub>3</sub> .. ..	116	22.2	0.191	0.178	Kp.				
Ca $\frac{1}{2}$ Mg $\frac{1}{2}$ Si O <sub>3</sub> .. ..	108	22.2	0.205	0.191	N.	0.186	Kp.		
Cu Si O <sub>3</sub> . H <sub>2</sub> O .. ..	157.4	30.8	0.195	0.182	Kp.				
Mg $\frac{2}{3}$ Fe $\frac{1}{3}$ Si O <sub>4</sub> .. ..	145.8	32.6	0.223	0.206	N.	0.189	Kp.		
Al <sub>3</sub> K <sub>3</sub> Si <sub>6</sub> O <sub>16</sub> .. ..	557	112.4	0.202	0.191	N.	0.183	Kp.		
Al <sub>2</sub> Na <sub>2</sub> Si <sub>6</sub> O <sub>16</sub> .. ..	524.8	112.4	0.214	0.196	N.	0.190	Kp.		

108. *Borates, Molybdates, Tungstates, Chromates and Sulphates.*  
(Compare § 87.)

K B O <sub>2</sub> .. ..	82	17.1	0.209	0.205	R.				
Na B O <sub>2</sub> .. ..	65.9	17.1	0.260	0.257	R.				
Pb B <sub>2</sub> O <sub>4</sub> .. ..	292.8	27.8	0.0949	0.0905	R.				
Pb B <sub>4</sub> O <sub>7</sub> .. ..	362.6	45.2	0.124	0.114	R.				
K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .. ..	233.8	51.6	0.221	0.220	R.				
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .. ..	201.6	51.6	0.256	0.238	R.	0.229	Kp.		
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> . 10 H <sub>2</sub> O .. ..	381.6	137.6	0.366	0.365	Kp.				
Pb Mo O <sub>4</sub> .. ..	367	28.8	0.0785	0.0827	Kp.				
Ca W O <sub>4</sub> .. ..	288	28.8	0.100	0.0967	Kp.				
Fe $\frac{2}{3}$ Mn $\frac{1}{3}$ W O <sub>4</sub> .. ..	303.4	28.8	0.0949	0.0978	R.	0.0930	Kp.		
Pb Cr O <sub>4</sub> .. ..	323.2	28.8	0.0891	0.0900	Kp.				
K <sub>2</sub> Cr O <sub>4</sub> .. ..	194.4	35.2	0.181	0.185	R.	0.189	Kp.		
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .. ..	294.6	53.6	0.182	0.189	R.	0.186	Kp.		
K H S O <sub>4</sub> .. ..	136.1	30.1	0.221	0.244	Kp.				
K <sub>2</sub> S O <sub>4</sub> .. ..	174.2	34.2	0.196	0.190	R.	0.196	Kp.		
Na <sub>2</sub> S O <sub>4</sub> .. ..	142	34.2	0.241	0.231	R.	0.227	Kp.		
N <sub>2</sub> H <sub>8</sub> S O <sub>4</sub> .. ..	132	52.6	0.398	0.350	Kp.				
Ba S O <sub>4</sub> .. ..	233	27.8	0.119	0.109	N.	0.113	R.	0.108	Kp.
Ca S O <sub>4</sub> .. ..	136	27.8	0.204	0.197	R.	0.185	N.	0.178	Kp.
Cu S O <sub>4</sub> .. ..	159.4	27.8	0.174	0.184	Pp.				
Mg S O <sub>4</sub> .. ..	120	27.8	0.232	0.222	R.	0.225	Pp.		
Mn S O <sub>4</sub> .. ..	151	27.8	0.184	0.182	Pp.				
Pb S O <sub>4</sub> .. ..	303	27.8	0.0917	0.0872	R.	0.0848	N.	0.0822	Kp.
Ir S O <sub>4</sub> .. ..	183.6	27.8	0.151	0.143	R.	0.136	N.	0.135	Kp.
Zn S O <sub>4</sub> .. ..	161.2	27.8	0.172	0.174	Pp.				
Cu S O <sub>4</sub> . H <sub>2</sub> O .. ..	177.4	36.4	0.205	0.202	Pp.				
Mg S O <sub>4</sub> . H <sub>2</sub> O .. ..	138	36.4	0.264	0.264	Pp.				
Zn S O <sub>4</sub> . H <sub>2</sub> O .. ..	179.2	36.4	0.203	0.202	Pp.				
Ca S O <sub>4</sub> . 2 H <sub>2</sub> O .. ..	172	45.0	0.262	0.273	N.	0.259	Kp.		
Cu S O <sub>4</sub> . 2 H <sub>2</sub> O .. ..	195.4	45.0	0.230	0.212	Pp.				
Zn S O <sub>4</sub> . 2 H <sub>2</sub> O .. ..	197.2	45.0	0.228	0.224	Pp.				
Fe S O <sub>4</sub> . 3 H <sub>2</sub> O .. ..	206	53.6	0.260	0.247	Pp.				
Cu S O <sub>4</sub> . 5 H <sub>2</sub> O .. ..	249.4	70.8	0.284	0.285	Kp.	0.316	Pp.		
Mn S O <sub>4</sub> . 5 H <sub>2</sub> O .. ..	241	70.8	0.294	0.323	Kp.	0.338	Pp.		
Ni S O <sub>4</sub> . 6 H <sub>2</sub> O .. ..	262.8	79.4	0.302	0.313	Kp.				
Co S O <sub>4</sub> . 7 H <sub>2</sub> O .. ..	280.8	88.0	0.313	0.343	Kp.				
Fe S O <sub>4</sub> . 7 H <sub>2</sub> O .. ..	278	88.0	0.317	0.346	Kp.	3.356	Pp.		

	Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.		
Mg S O <sub>4</sub> . 7 H <sub>2</sub> O ..	246	88.0	0.358	0.362	Kp.	0.407 Pp.
Ni S O <sub>4</sub> . 7 H <sub>2</sub> O ..	280.8	88.0	0.313	0.341	Pp.	
Zn S O <sub>4</sub> . 7 H <sub>2</sub> O ..	287.2	88.0	0.306	0.347	Kp.	0.328 Pp.
Mg K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> . 6 H <sub>2</sub> O ..	402.2	113.6	0.282	0.264	Kp.	
Ni K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> . 6 H <sub>2</sub> O ..	437	113.6	0.260	0.245	Kp.	
Zn K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> . 6 H <sub>2</sub> O ..	443.4	113.6	0.256	0.270	Kp.	
Al <sub>2</sub> K <sub>2</sub> S <sub>4</sub> O <sub>16</sub> . 54 H <sub>2</sub> O ..	949	317.6	0.335	0.371	Kp.	
Cr <sub>2</sub> K <sub>2</sub> S <sub>4</sub> O <sub>16</sub> . 24 H <sub>2</sub> O ..	998.6	317.6	3.318	0.324	Kp.	

109. *Arseniates, Phosphates, Pyrophosphates, and Metaphosphates, Nitrates, Chlorates, Perchlorates, and Permanganates.* (Compare § 88.)

K As O <sub>3</sub> .. ..	162.1	24.8	0.153	0.156	R.	
K H <sub>2</sub> As O <sub>4</sub> .. ..	180.1	33.4	0.185	0.175	Kp.	
Pb <sub>2</sub> As <sub>2</sub> O <sub>8</sub> .. ..	899	64.0	0.0712	0.0728	R.	
Ag <sub>3</sub> P O <sub>4</sub> .. ..	419	40.6	0.0969	0.0896 ?	Kp.	
K H <sub>2</sub> P O <sub>4</sub> .. ..	136.1	32.4	0.238	0.208	Kp.	
Na <sub>2</sub> H P O <sub>4</sub> . 12 H <sub>2</sub> O ..	358	139.7	0.390	0.408	Pr.	
Pb <sub>3</sub> P <sub>2</sub> O <sub>8</sub> .. ..	811	62.0	0.0764	0.0798	R.	
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .. ..	330.4	64.4	0.195	0.191	R.	
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .. ..	266	64.4	0.242	0.228	R.	
Pb <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .. ..	588	51.6	0.0878	0.0821	R.	
Na P O <sub>3</sub> .. ..	102	23.8	0.233	0.217	Kp.	
Ca P <sub>2</sub> O <sub>6</sub> .. ..	198	41.2	0.208	0.199	R.	
Ag N O <sub>3</sub> .. ..	170	24.8	0.146	0.144	R.	
K N O <sub>3</sub> .. ..	101.1	24.8	0.245	0.239	R.	0.230 Kp.
K $\frac{1}{2}$ Na $\frac{1}{2}$ N O <sub>3</sub> .. ..	93	24.8	0.267	0.235	Pr.	
Na N O <sub>3</sub> .. ..	85	24.8	0.292	0.278	R.	0.257 Kp.
N <sub>2</sub> H <sub>4</sub> O <sub>3</sub> .. ..	80	34.0	0.425	0.455	Kp.	
Ba N <sub>2</sub> O <sub>6</sub> .. ..	261	43.2	0.166	0.152	R.	0.145 Kp.
Pb N <sub>2</sub> O <sub>6</sub> .. ..	331	43.2	0.130	0.110	Kp.	
Sr N <sub>2</sub> O <sub>6</sub> .. ..	211.6	43.2	0.204	0.181	Kp.	
K Cl O <sub>3</sub> .. ..	122.6	24.8	0.202	0.210	R.	0.194 Kp.
Ba Cl <sub>2</sub> O <sub>6</sub> . H <sub>2</sub> O ..	322	51.8	0.161	0.157	Kp.	
K Cl O <sub>4</sub> .. ..	138.6	28.8	0.208	0.190	Kp.	
K Mn O <sub>4</sub> .. ..	158.1	28.8	0.182	0.179	Kp.	

110. *Organic Compounds.* (Compare § 89.)

	Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.		
Cyanide of mercury	Hg C <sub>2</sub> N <sub>2</sub> .. ..	252	22.8	0.091	0.100	Kp.
"    zinc and potassium	Zn K <sub>2</sub> C <sub>4</sub> N <sub>4</sub> .. ..	247.4	52.0	0.210	0.241	Kp.
Ferrocyanide of potassium ..	Fe K <sub>3</sub> C <sub>6</sub> N <sub>6</sub> .. ..	329.3	74.8	0.227	0.233	Kp.
Ferricyanide of potassium ..	Fe <sub>4</sub> K <sub>4</sub> C <sub>6</sub> N <sub>6</sub> . 3 H <sub>2</sub> O ..	422.4	107.0	0.253	0.280	Kp.
Chloride of carbon.	C <sub>2</sub> Cl <sub>6</sub> .. ..	237	42.0	0.177	0.178	Kp.
Naphthalene ..	C <sub>10</sub> H <sub>8</sub> .. ..	128	36.4	0.234	0.310	A.

				Atomic weight.	Atomic heat. Calculated.	Specific heat. Calculated.	Specific heat. Observed.	
Cerotic acid	..	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	..	410	108.8	0.441	} 0.429	Pr.
Palmitate of melis- syle ..	..	C <sub>46</sub> H <sub>92</sub> O <sub>2</sub>	..	676	302.4	0.447		
Cane-sugar	..	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	..	342	116.2	0.340	0.301	Kp.
Mannite	..	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	..	182	67.0	0.368	0.324	Kp.
Succinic acid	..	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> ..	..	118	37.0	0.314	0.313	Kp.
Tartaric acid	..	C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> ..	..	150	45.0	0.300	0.288	Kp.
Racemic acid	..	C <sub>2</sub> H <sub>6</sub> O <sub>6</sub> . H <sub>2</sub> O ..	..	168	53.6	0.319	0.319	Kp.
Formiate of barium..	..	C <sub>2</sub> H <sub>2</sub> Ba O <sub>4</sub>	..	227	30.6	0.135	3.143	Kp.
Oxalate of potassium.	..	C <sub>2</sub> K <sub>2</sub> O <sub>4</sub> . H <sub>2</sub> O ..	..	184.2	41.0	0.223	0.236	Kp.
Quadroxalate of pot- ass ..	..	C <sub>2</sub> H <sub>3</sub> K O <sub>8</sub> . 2 H O	..	254.1	69.7	0.274	0.283	Kp.
Bitartrate of potassium	..	C <sub>4</sub> H <sub>5</sub> K O <sub>6</sub>	..	188.1	49.1	0.261	0.257	Kp.
Seignette salt	..	C <sub>4</sub> H <sub>4</sub> Na K O <sub>6</sub> . 4 H <sub>2</sub> O	..	282.1	87.6	0.311	0.328	Kp.
Bimalate of potassium	..	C <sub>8</sub> H <sub>10</sub> Ca O <sub>10</sub> . 8 H <sub>2</sub> O	..	450	152.6	0.339	0.338	Kp.

111. The preceding synopsis shows, for the great majority of substances contained in it, an adequate agreement between the observed specific heats and those calculated on such simple assumptions. In estimating the differences, the extent must be remembered to which various observers differ for the same substance. It must be considered that the present better determinations of the specific heat, even those made by the same experimenter, for substances where it may be expected that Neumann's law applies, do not agree exactly with it, not more nearly than within  $\frac{1}{10}$  or  $\frac{1}{5}$  of the value; and that for those elements which are considered here as obeying Dulong and Petit's law, even greater deviations occur between the numbers found experimentally and those to be expected on the assumption of the universal validity of this law. (These deviations, *i.e.* the differences between the atomic heats found for these elements, are seen from § 82.) The extent to which the experimentally determined specific heats deviate from such a law, Neumann's for instance, in bodies for which calculation takes it as applying, gives, of course, the means of judging what differences may occur between the observed and calculated numbers without invalidating the admissibility of the calculation attempted. And it is as much a matter of course that, in those bodies in which a marked deviation from Neumann's law has been already mentioned (compare § 95), a greater difference is found in the present synopsis between calculation and observation.

I consider the agreement between calculation and observation,

as shown in the synopsis § 103 to 110, as in general sufficient for a first attempt of that kind. But it need scarcely be mentioned that I by no means consider the calculated as more accurate than the observed numbers, or among several numbers consider that the most accurate which is nearest the calculated; for that, the bases of calculation are much too uncertain. The list of atomic heats given at the commencement of § 103 is scarcely much more accurate than were the first tables of atomic weights; but just as the latter have experienced continual improvements, and thus what was at first only an approximate agreement between the calculated and observed composition of bodies, has been brought within considerably narrower limits, and apparent exceptions have been explained, so, in like manner, will this be the case for ascertaining what atomic heats are to be assigned to the elements, and how the atomic heats of compounds may be deduced therefrom. This much, however, may even now be said, that while formerly for many solid substances, a statement of the specific heat could in no way be controlled, a concealed source of error for the determination of this property was not indicated, and an error which materially altered the number for this property could not be recognised, at present, even if only roughly, such a control is possible. Compare § 77.

PART VI.—*Considerations on the Nature of the Chemical Elements.*

112. The proof given in the preceding that Dulong and Petit's law is not universally valid, justifies certain conclusions, in reference to the nature of the so-called chemical elements, which may here be developed.

What bodies are to be regarded as chemical elements? Does the mere fact of nondecomposibility determine this? or may a body be nondecomposable in point of fact, and yet, from reasons of analogy, be regarded, not as an element but as a compound? The history of chemistry furnishes numerous examples of cases in which sometimes one and sometimes another mode of view led to results which at present are regarded as accurate. The earths were in 1789 non-decomposable in point of fact, when Lavoisier expressed the opinion that they were compounds, oxides of unknown metals. Lavoisier's argumentation was based on the fact that the earths enter as bases into salts, and that it was to be assumed in regard

to all salts, that they contained an oxygen-acid and an oxygen-base. But the view, founded on the same basis, that common salt contains oxygen, and the subsequent view that what is now called chlorine contained a further quantity of oxygen besides the elements of an oxygen-acid, did not find an equally permanent recognition. On the basis of the actual nondecomposibility of chlorine, Davy, from about 1810, maintained its elementary character; and this view has become general, especially since Berzelius, after a long struggle against it, adopted it, more I think because he was out-voted than because he was convinced.

Almost all chemists of the present time consider chlorine, and in conformity therewith, bromine and iodine, as elementary bodies; but we know with what persistence Schönbein attacks this view, and adheres to the opinion that these bodies are oxygen-compounds, peroxides of unknown elements. Is there anything which enables us to decide with greater certainty on the elementary nature of chlorine and the analogous bodies than has hitherto been the case?

No one can maintain that the bodies which chemists regard as elements are absolutely simple substances. We are compelled to admit the possibility that they may be decomposed into still simpler bodies; how far a body is to be regarded as an element, is so far relative, that it depends on the development of the means of decomposition which practical chemistry has at its disposal, and on the trustworthiness of the conclusions which theoretical chemistry can deduce. A discussion as to whether chlorine or iodine is an elementary body can be taken only in the sense whether chlorine is as simple a body as oxygen or manganese, or nitrogen; or whether it is a compound body, as peroxide of manganese or peroxide of hydrogen for example.

If Dulong and Petit's law were universally valid, it would indicate, not merely for chemical elements a relation between the atomic weight and the specific heat in the solid state, but it could be used as a test for the elementary nature of a body whose atomic weight is known. That iodine, from a direct determination, and chlorine by an indirect determination of specific heat, had atomic heats agreeing with Dulong and Petit's law, would be a proof that iodine and chlorine, if compounds at all, are not more so than other so-called elements for which this law is regarded as valid.

According to Neumann's law, compounds of analogous atomic

composition have approximately the same atomic heats. In general, bodies whose atom consists of a relatively greater number of non-decomposable atoms, or is of more complicated composition, have greater atomic heats. In these compounds, more especially those whose elements all follow Dulong and Petit's law, magnitude of atomic heat is exactly a measure of the complexity or of the degree of composition (compare § 93). If Dulong and Petit's law were valid, it could be concluded with great positiveness that the so-called elements, if they are compounds of unknown and simpler substances, are compounds of the same order. It would be a remarkable result that the act of chemical decomposition had everywhere found its limit at such bodies as those which, if compound at all, have, with every difference of chemical deportment, the same degree of complexity. Imagine the simplest bodies, probably as yet unknown to us, the true chemical elements, forming a horizontal spreading layer, and piled above them, the simpler and then the more complicated compounds; the universal validity of Dulong and Petit's law would include the proof, that all elements at present assumed by chemists lay in the same layer, and that chemistry, in recognising hydrogen, oxygen, sulphur, chlorine, and the different metals as nondecomposable bodies, had penetrated to the same depth in that field of inquiry, and had found at the same depth the limit to its penetration.

This result I formerly propounded\* when I still believed in the validity of Dulong and Petit's law. But with the proof that this law is not universally true, the conclusion to which this result leads loses its justification. Starting now from the elements recognised in chemistry, we must rather admit that the magnitude of the atomic heat of a body depends, not only on the number of elementary atoms contained in one atom of it, or on the complexity of the composition, but also on the atomic heat of the elementary atoms entering into its composition; it appears now possible that a decomposable body may have the same atomic heat as a non-decomposable one.

To assume in chlorine the presence of oxygen, and to consider it as analogous to peroxide of manganese, or in general to the peroxide of a bi-equivalent element†, is less in accordance with

\* "Ueber die Verschiedenheit der Materie vom Standpunkt des Empirismus," eine academische Rede. Giessen, 1860; s. 15.

† I must not omit to mention that equivalent weights of iodine and peroxide of manganese have almost equal capacity for heat. As regards oxidizing action, 127 of

what is at present considered true in chemistry, than to consider it as the peroxide of a monoequivalent element, analogous to peroxide of hydrogen. It is remarkable that peroxide of hydrogen, in the solid state or in solid compounds, must have almost as great an atomic heat (for  $\text{HO } 2\cdot3 + 4 = 6\cdot3$ ) as those elements which obey Dulong and Petit's law, and especially as iodine, bromine, and chlorine, according to the direct and to the indirect determination of their atomic heat: the same must be the case for the analogous peroxides of such still unknown elements as have an atomic heat as great as that of hydrogen. As far as may be judged from its specific heat, chlorine *may* be such a peroxide; but this consideration shows no necessity for assuming that it actually is so.

In a great number of cases, the atomic heat of compounds gives more or less accurately a measure for the degree of complexity of their composition.\* And this is the case also with such compounds as are comparable in their chemical department with undecomposed bodies. If cyanogen or ammonium had not been decomposed, or could not be so with the means at present offered by chemistry, the greater atomic heats of their compounds, compared with those of analogous chlorine or potassium-compounds (compare § 96), and of cyanogen and ammonium as compared with chlorine and potassium, would indicate the more complex nature of those so-called compound radicals. The conclusion appears admissible that for the so-called elements the directly or indirectly ascertained atomic heats are a measure for the complexity of their composition. Carbon and hydrogen, for example, if not themselves simple bodies, are more so than silicium or oxygen; and still more complex compounds are the elements which are now considered as following Dulong and Petit's law; with the restriction, however, that for these also the atomic heats may be more accurately determined and differences proved in them

iodine corresponds to 43·5 peroxide of manganese; Regnault found the specific heat of the former = 0·0541; I found that of the latter = 159;

$$127 \times 0\cdot0541 = 6\cdot87; 43\cdot5 \times 0\cdot159 = 6\cdot92.$$

\* The differences in the atomic heats of the elements are of course most distinctly seen in their free state, but in their analogous compounds these differences are the less prominent the more complex the compounds, that is, the greater the number of atoms of the same kind and the same atomic heat which are united to those elementary atoms whose atomic heat is assumed to be unequal. The difference in the atomic heats of C and As, for instance (1·8 and 6·4), is relatively far greater than for  $\text{CaCO}_3$  and  $\text{KAsO}_3$  (20·2 and 24·8).



which justify similar conclusions.\* One might be tempted, by comparing atomic heats, to form an idea how the more complex of the present non-decomposable bodies might be composed of more simple ones, just as such a comparison has been shown to be possible for chlorine; but it is at once seen that to carry out such an attempt, the atomic heats of the elements, especially those which can only be indirectly determined, are not settled with adequate certainty.

It may appear surprising, or even improbable, that so-called elements which can replace each other in compounds, as, for instance, hydrogen and the metals, or which enter into compounds as isomorphous constituents, like silicium and tin, should possess unequal atomic heats and unequal complexity of composition. But this is not more surprising than that undecomposable bodies, and those which can be proved to be compound, as, for example, hydrogen and nitric peroxide, or potassium and ammonium, should replace one another, preserving the chemical character of the compounds, and even be contained as corresponding constituents in isomorphous compounds.

I have here expressed suppositions with reference to the nature of the so-called elements which appear to me based on trustworthy conclusions from well-proved principles. It is in the nature of the case that the certain basis of fact and of what can be empirically demonstrated must be left. It must also not be forgotten that these conclusions only allow something to be supposed as to which of the present non-decomposable bodies are more complex and which of simpler composition, and nothing as to the question what simpler substances may be contained in the more complex ones. The consideration of the atomic heats may indicate something as to the structure of a compound atom, but in general gives no clue as to the qualitative nature of the simpler substances used in the construction of the more complex atoms. But even if these suppositions are not free from uncertainty and imperfection, they appear worthy of attention in a subject which, for science, is still so much in darkness, as is the nature of the non-decomposable bodies.

\* It is possible, for example, that certain non-decomposable bodies which only approximately obey Dulong and Petit's law, are analogous compounds of simpler substances of essentially different atomic heat: the approximate agreement of the atomic heats of such non-decomposable bodies would then depend on a reason similar to that which has been given for the atomic heats of  $\text{CaCO}_3$  and  $\text{KAsO}_3$ . (Compare the previous note.)