



XXVII. On the heat evolved or absorbed when a liquid is brought in contact with a finely divided solid

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To cite this article: G.J. Parks (1902) XXVII. On the heat evolved or absorbed when a liquid is brought in contact with a finely divided solid , Philosophical Magazine Series 6, 4:20, 240-253, DOI: [10.1080/14786440209462841](https://doi.org/10.1080/14786440209462841)

To link to this article: <http://dx.doi.org/10.1080/14786440209462841>



Published online: 15 Apr 2009.



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The enlargement necessary to carry the wheel may be conveniently made circular (at least in the portion remote from A) round the point B as centre. In this case it will be easily moved along a ruling-edge set parallel to the motion of B.

The bar may be graduated in units of b from the point B as zero, and the slotted pin-head may have a vernier for reading $\cosh \theta$. Of course CB on the same scale will be $\sinh \theta$.

XXVII. *On the Heat Evolved or Absorbed when a Liquid is brought in contact with a Finely Divided Solid.* By G. J. PARKS *.

I. INTRODUCTION.

POUILLET † discovered the fact that when a powder is put into a liquid which does not exert any solvent or chemical action upon it, there is a rise of temperature. In some of the experiments made by Pouillet with mineral substances, the rise of temperature varied from 3° to 1° C. This discovery was confirmed by several other investigators, but nearly all the earlier observations were merely thermometric, and are therefore of little value for purposes of comparison, since the rise of temperature must obviously depend on the thermal capacity of the whole mass throughout which the heat is distributed. In fact, by suitably varying the conditions of the experiment it has been found possible to obtain any rise of temperature up to 30° C. or more.

Junck ‡ found that when sand is placed in water the temperature of which is above 4° C. there is a rise of temperature, and when the temperature of the water is below 4° C. there is a fall of temperature. This is quite in accordance with what would be expected on the supposition that the *Pouillet effect* is due to a pressure at the surface of the powder, and the variation of pressure for a given variation of temperature can be calculated from the equation

$$dp = \frac{J \cdot c \cdot \rho}{\tau \cdot \alpha} \cdot d\tau,$$

where α is the coefficient of expansion of the liquid at constant pressure, ρ the density, c the specific heat, τ the absolute temperature, and J the mechanical equivalent of heat.

Meissner § showed that when certain powders are placed

* Communicated by the Physical Society: read June 20, 1902.

† Pouillet, *Ann. de Chim. et de Physique*, xx. p. 141 (1822).

‡ Junck, *Pogg. Ann.* cxxv. p. 292 (1865).

§ Meissner, *Wied. Ann.* xxix. p. 114 (1886).

in water at a temperature below 4° C., a rise of temperature is observed, and he accordingly rejected the physical hypothesis of surface pressure, and adopted a chemical or physico-chemical hypothesis which had been advanced by Cantoni*, and which has been more fully developed by Martini†. It has, however, been pointed out that the experiments of Meissner do not disprove the validity of the hypothesis of surface pressure, for as the pressure increases the point of maximum density of water is lowered, and at a pressure of about 200 atmospheres the point of maximum density of water is at or near 0° C., as shown by Tait, Amagat, Lussana, and others‡.

Lagergren§ has shown that the pressure at the surface of silica and water would, from the above equation, amount to some thousands of atmospheres.

Martini, on the other hand, is unwilling to admit such an enormous pressure at the surface, and he supposes that, just as some solids are dissolved by liquids and thereby become liquid, so liquids are absorbed by powders and thereby become solid, the heat evolved being equivalent to the latent heat which the liquid gives up in solidifying.

Other investigators who have made experiments on the Pouillet effect and allied phenomena are Tate||, Melsens¶, Chappuis**, Wiedemann and Lüdeking††, Gore‡‡, Ercolini§§, Bellati|||, and Linebarger¶¶.

In Gore's experiments, a powder such as silica or alumina was dropped from the air into water which contained some soluble salt; the liquid was not stirred, and the temperature observed was that of the powder which sank to the bottom of the liquid. The object of these experiments was to discover

* Cantoni, *Rend. del R. Istituto Lombardo*, viii. p. 135 (1866).

† Martini, *Atti del R. Istituto Veneto*, viii. (1896); ix. (1897); xii. (1900).

‡ Tait, *Proc. R. Soc. of Edinburgh*, 1881-82, 1882-83; Marshall, Smith and Omond, *Proc. Roy. Soc. Edinburgh*, 1881-82; Amagat, *Comptes Rendus*, cxvi. p. 946 (1893); Lussana, *Nuovo Cimento* (4) ii. p. 233 (1895).

§ Lagergren, *Kongl. Vetenskaps Akademiens*, B. 24, Afd. ii., Stockholm, 1899.

|| Tate, *Phil. Mag.* [4] xx. p. 508 (1860).

¶ Melsens, *Mémoires de l'Académie de Belgique*, xxiii. (1873); *Ann. de Chim. et de Phys.* [5] iii. p. 522 (1874).

** Chappuis, *Wied. Ann.* xix. p. 21 (1883).

†† Wiedemann and Lüdeking, *Wied. Ann.* xxv. p. 145 (1885).

‡‡ Gore, *Phil. Mag.* xxxvii. p. 306 (1894); *Birm. Phil. Soc. Proc.* vol. ix. pt. 1 (1893).

§§ Ercolini, *Nuovo Cimenti*, Serie 4, vol. ix., Feb. 1899.

||| Bellati, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda, 1900.

¶¶ Linebarger, *Physical Review*, vol. xiii. No. 1, July 1901.

the influence of the substance in solution; and in fact the whole research was the outcome of another investigation in which Dr. Gore showed that a powder has the property of abstracting from a liquid part of the substance in solution. One remark of Dr. Gore bears on the present investigation: having made observations on precipitated silica and sand, he states that the action is purely a surface one, and he suggests that if the relation between the rise of temperature and the area of the surface were known, the method could be employed to obtain the area of the surface of a powder.

Prof. FitzGerald* regarded the Pouillet effect as due to a pressure at the surface of the powder and the liquid; he suggested the application of the laws of thermodynamics, and he pointed out the need of further investigation and quantitative treatment.

Notwithstanding the large number of observations which have been made in connexion with this phenomenon, there are no data by means of which we are enabled to express the quantity of heat evolved as a function of the area of the surface. The experiments of Martini, Ercolini, and others show that for the *same* powder and liquid the quantity of heat evolved is proportional to the mass of the powder used in the experiment, but no attempts have been made to calculate the area of the surface exposed to the liquid. The equation used by

Ercolini is $M + pc - \frac{p}{\theta} \cdot k = 0$, where M is the mass of the water, including the water equivalent of the calorimeter, p is the mass of the powder, and c the specific heat of the powder, θ is the observed rise of temperature, k is a constant and represents the amount of heat evolved on putting one gram of the powder into water.

The value of k is, however, not really constant, but diminishes very slightly as p increases. Martini explains this on the supposition that some of the water is solidified on the powder and its specific heat is thereby reduced to $\cdot 5$. Bellati has, however, shown by direct experiment that this supposition is wrong. Some silica was well dried, and then exposed to aqueous vapour so that it absorbed moisture, the mass of which was determined by weighing the silica before and after its exposure; the specific heat of the water was then found by means of a Bunsen's ice-calorimeter, an assumed value being taken for the specific heat of silica. The specific heat of the water was found to be much greater than $\cdot 5$, and it did not differ very much from 1.

* FitzGerald, 'Nature,' vol. xlix. pp. 293, 316 (1894).

It seems highly probable that the specific heat of the water close to the surface of the silica differs from the specific heat of the water which is farther away from the surface, but any attempt to distinguish clearly between the two must necessarily lead to some doubtful assumptions. A consideration of the Pouillet effect is, however, incomplete if the possibility of such a variation in the specific heat of the liquid is not taken into account. There is also another possible source of variation in the quantity of heat evolved, which none of the investigators have considered, namely, the variation of the heat evolved with the temperature. In many of the records of experiments the initial temperature of the calorimeter is not even stated, and in other cases, where the temperatures are recorded, it is impossible to decide whether the variations in the quantity of heat evolved depend upon differences in the initial temperature of the liquid and powder, or upon change of specific heat of the liquid, or upon some cause of error in the experiment.

The objects of the present investigation were to obtain a relation between the quantity of heat evolved and the area of the surface exposed, to find the rate of variation of heat evolved with variation of temperature, and to apply to the results the laws of thermodynamics.

The nearest approach to a relation connecting the quantity of heat evolved with area of surface is the statement of Mr. Linebarger, that the finer the powder the greater the heat effect, and in the case of water and silica the heat effect is about proportional to the fineness of the powder. This conclusion is based upon a very few experiments with two samples of silica of different degrees of fineness, and it is directly opposed to the views of Martini, who states that the fineness of the powder does not influence the result to any important extent*.

II.

On the Relation between the Area of Surface of Silica and the Heat evolved on bringing the Surface in contact with Water.

In making any experiment on the Pouillet effect, it is essential that the powder should be perfectly dry and that it should be at exactly the same temperature as the liquid. Very few of the investigators have succeeded in securing these

* Martini, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda (1900), p. 622 (Non è dunque la sottigliezza dei granuli della polvere che influisca in modo sostanziale sul fenomeno come ce lo provano le tre qualità di carbonato di calce).

conditions, but Mr. Linebarger's methods seem to leave nothing to be desired, and the experiments now to be described were made in a similar way.

The precipitated silica, sand, or other substance to be experimented upon, was heated in an evaporating dish to dull red-heat. A test-tube was drawn out to a narrow neck at about seven or eight centimetres from the closed end, and the tube was then weighed. Some of the powder was now placed in the tube while it was still hot, and the tube was connected to an air-pump, and the air was exhausted as completely as possible, the powder being at the same time heated until the tube showed signs of softening and closing in under the atmospheric pressure. The bulb was now sealed at the narrow neck, and when cold the whole of the tube and the powder were weighed together; the difference between this weighing and the first weighing gave the mass of the powder, and a third weighing gave the mass of bulb and powder.

The calorimeter used in these experiments was a copper vessel, 9 cm. in height and 7.5 cm. in diameter; it weighed 104.605 grammes, and its water equivalent was 9.95 grammes. This was suspended by silken threads inside another copper vessel, this again was placed in a glass beaker containing water, and the glass beaker was placed inside another glass beaker, the space between the two beakers being filled with "glass wool" or "cotton silicate," which is a very bad conductor of heat. The whole apparatus was kept in a cupboard with glass doors. The temperature of the calorimeter could therefore be kept constant for a considerable time.

The thermometers were divided to $\cdot 02^{\circ}$ C., and the readings were taken to the tenth of a division, so that there was a possible error in each reading of not more than $\cdot 002^{\circ}$ C.

An instrument was used to serve the purpose of crushing the bulb, thus liberating the powder under the surface of the water, and it also served as a stirrer to keep the temperature of the water uniform. A piece of brass tubing about an inch in diameter was filed away in the middle, thus leaving two rings at the ends about an inch apart and connected by that part of the tube between them which had not been filed away. A nut was soldered on to the tube between the rings and a screw worked in the nut, the axis of the screw being at right angles to the axis of the tube, so that when the glass bulb was placed in the tube it was held firmly by the screw pressing against it, and a few more turns of the screw were sufficient to break the bulb. The top of the screw was flattened to a sharp edge, which engaged in a split at the end of a stout brass wire; this wire could thus be used to turn the screw,

and then could be immediately removed. A piece of glass tubing was attached to the brass tube so that the screw worked along the axis of the glass tube, which served as a handle of non-conducting material. The water equivalent of this instrument was 2.35 grammes, and that of each thermometer was 1.50 grammes.

In making an experiment, the bulb containing the powder was placed under the surface of the water in the calorimeter, and allowed to remain there for some hours, generally about twenty-four hours. The temperature was then observed every five minutes, and if several consecutive readings were the same, the bulb was broken, and the temperature again observed until it was constant. The rise of temperature was generally complete in three minutes or less, the liquid being gently stirred together with the powder.

The mass of water, M , was always large compared with the mass of the powder, p , and hence the error, if any, involved in taking the specific heat of the water as 1, must have been exceedingly small. The temperatures at which the experiments were made did not differ very much, and the variation due to these small differences of temperature was neglected; from theoretical considerations it follows that the variation in the heat evolved is not more than .3 per cent. per degree centigrade, and later experiments tend to confirm this.

The specific heat of the glass bulb and its contents was taken as .19; any error in this assumption could not have affected the results, since the mass of the bulb and its contents was always small compared with the mass of water.

The average diameter of the grains of powder was obtained by measuring many hundreds of grains by means of a microscope supplied with stage micrometer and eyepiece micrometer. The microscope was so adjusted that thirty divisions of the eyepiece micrometer exactly corresponded to one tenth of a millimetre on the stage micrometer, so that one division of the eyepiece micrometer represented $\frac{1}{3000}$ cm. It was found that in the dry state the smaller grains of powder were often joined together, forming larger grains, and it was not easy to distinguish a lump consisting of several small grains from a complete grain; hence any measurements of powder in the dry state are likely to make the powder appear much coarser than it really is. When the powder was put in a drop of water on a glass slide under the microscope and stirred with a small brush, the larger pieces of silica were seen to break up into smaller grains of fairly uniform size. The average diameter of the grains was

found to be $\frac{3}{4}$ of a division of the eyepiece micrometer, that is $\cdot 00025$ cm. Suppose now there are n such average grains to a gramme of powder, then, since the specific gravity of the powder is 2.2, we have

$$n \times \frac{\pi}{6} (\cdot 00025)^3 \times 2.2 = 1$$

on the assumption that the grains are spherical, and the area of surface is equal to

$$n \cdot \pi (\cdot 00025)^2 = 6 \times \frac{1}{2.2} \times \frac{1}{\cdot 00025} = 10900 \text{ sq. cm.}$$

That is, one gramme of the precipitated silica exposed a surface of about 10900 sq. cm. Another variety of silica used in these experiments was examined under the microscope, and the average diameter of the grains was found to be 1.2 divisions or $\cdot 00040$ cm., so that the area of surface per gramme was

$$6 \times \frac{1}{\cdot 0004} \times \frac{1}{2.2} = 6820 \text{ sq. cm.}$$

Experiments were also made with some fine grey sand of specific gravity 2.6; the average diameter of the grains was $\cdot 010$ cm., and the area of the surface exposed by one gramme of the sand was therefore

$$6 \times \frac{1}{2.6} \times \frac{1}{\cdot 01} = 231 \text{ sq. cm.,}$$

on the assumption that the grains were spherical.

The probable error in estimating the surface of a powder by this method is considerable, because the particles are irregular in shape and size, especially those of the sand. Experiments were therefore made with "cotton silicate" or "glass wool," a kind of glass of specific gravity 2.7, in the form of fine filaments which, when examined under the microscope, are seen to be almost perfect cylinders, of fairly uniform size. The length of each cylindrical filament was very great compared with its diameter, so that in calculating the area of its surface only the curved surface was considered. The average diameter was found to be $\cdot 00175$ cm.; hence the area of surface exposed by one gramme of the silicate was

$$\frac{4}{2.7 \times \cdot 00175} = 847 \text{ sq. cm.}$$

The accompanying table (I.) shows the results of some of the experiments. Other experiments were made, but the results are not shown because they are considered to be

unreliable. In several experiments, there was a slight crack in the bulb before it was placed in the calorimeter, and in these instances the result obtained was far too low, though the crack was not large enough to admit any visible quantity of water; this shows the great importance of keeping the powder dry until the moment of the experiment. Other experiments were rejected because there was a rapid variation in the temperature of the room at the time, so that the final temperature of the calorimeter did not reach a constant value until long after the time usually occupied in making an experiment. The rise of temperature observed in the experiments with sand and cotton silicate was only about $\frac{1}{30}^{\circ}\text{C.}$, and hence the results are only given to the second significant figure.

TABLE I.

Number of Experiment.	Nature of Substance.	Diameter (cm.).	Estimated area of surface per gramme.	Mass of substance in grammes.	Mass of bulb.	Mass of water including water-equivalent of calorimeter, powder, bulb, thermometer, and stirrer.	Initial Temperature (Centigrade).	Rise of Temperature.	Calories per gramme of the substance.	Calories per sq. cm. of the surface.
1.	Silica (precipitated)	·00025	10900	3·749	3·34	205·51	6·334	·208	11·4	·00105
2.	" "	" "	" "	3·563	3·55	210·31	6·552	·192	11·3	·00104
3.	" "	" "	" "	4·169	3·61	210·05	7·012	·222	11·2	·00103
4.	" "	" "	" "	4·037	3·53	239·74	7·586	·194	11·5	·00105
5.*	" "	·00040	6820	3·940	4·03	207·26	7·320	·136	7·15	·00105
6.	Sand	·010	231	20·050	3·70	220·03	5·400	·022	·24	·0010
7.	" "	" "	" "	20·589	4·57	240·10	5·482	·020	·23	·0010
8.	" "	" "	" "	22·033	3·81	252·28	8·320	·020	·23	·0010
9.	" "	" "	" "	20·188	4·14	255·15	9·228	·018	·23	·0010
10.	Silicate (cylindrical filaments)	·00175	847	2·240	3·81	200·10	5·742	·010	·89	·0011
11.	" "	" "	" "	4·006	3·50	210·93	5·722	·018	·95	·0011
12.	" "	" "	" "	4·138	3·47	211·75	6·052	·018	·92	·0011

* See Table II. for results of other experiments with silica.

It is considered that these results justify the enunciation of the following law :—

“ When silica, sand, or glass, is brought in contact with water, at approximately constant temperature, the heat evolved is proportional to the area of the surface exposed by the solid, and the amount of heat developed per square centimetre is approximately ·00105 calorie when the temperature is near 7° C.

III.

Application of the Laws of Thermodynamics.

Assuming that the phenomenon of Pouillet is reversible, we may apply the laws of thermodynamics. Let h be the amount of heat developed per square centimetre at the surface of the solid and liquid at constant temperature, let c be the specific heat of the liquid when the surface remains constant, let s be the area of surface of the powder exposed to one gramme of the liquid, the volume of which is supposed to remain constant, let P be the surface-pressure for the given solid and liquid. Then, with the usual notation of thermodynamics,

$$dQ = c \cdot dt - h \cdot ds, \quad . \quad . \quad . \quad . \quad . \quad (i.)$$

and $dQ = \tau \cdot d\phi$, hence

$$\tau \cdot d\phi = c \cdot dt - h \cdot ds. \quad . \quad . \quad . \quad . \quad . \quad (ii.)$$

The variation of the internal energy is

$$dU = J \cdot dQ - P \cdot ds = J \cdot c \cdot dt - (J \cdot h + P) ds, \quad (iii.)$$

where J represents the mechanical equivalent of heat. Imposing the condition that the variation of the internal energy is a perfect differential, we obtain

$$J \left(\frac{dc}{ds} + \frac{dh}{dt} \right) = - \frac{dP}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (iv.)$$

Imposing the condition that the variation of entropy, $d\phi$, is a perfect differential, we obtain

$$\frac{dc}{ds} + \frac{dh}{dt} = \frac{h}{\tau}. \quad . \quad . \quad . \quad . \quad . \quad (v.)$$

From equations (iv.) and (v.) we have

$$h = - \frac{\tau}{J} \cdot \frac{dP}{dt} \quad . \quad . \quad . \quad . \quad . \quad (vi.)$$

and

$$\frac{dc}{ds} = \frac{\tau}{J} \cdot \frac{d^2P}{dt^2}. \quad . \quad . \quad . \quad . \quad . \quad (vii.)$$

Applying these equations to the results obtained for water and silica, we find that the surface-pressure diminishes with rise of temperature, for since heat is evolved when the surface of water and silica is extended, h is positive, and hence from equation (vi.) $\frac{dP}{dt}$ is negative. Taking h as .00105 when r is 280°

and $J = 4.2 \times 10^7$, we have $\frac{dP}{dt} = -157$; that is, at 7°C. the surface-pressure of water and silica diminishes at the rate of 157 dynes per cm. for an increase of temperature of 1°C.

From equation (v.) we have $\frac{dc}{ds} + \frac{dh}{dt} = \frac{.00105}{280} = .0000037$ at a temperature of 7°C.

From equation (v.) it is clear that if either $\frac{dc}{ds}$ or $\frac{dh}{dt}$ is known, the other can be found, and if *both* of these could be determined with precision, a value for absolute zero could be obtained, which would be independent of the air-thermometer.

IV.

On the Rate of Variation of the Heat evolved with Change of Temperature.

The accompanying Table II. shows the results of experiments made to determine, at least approximately, the value of

TABLE II.

Experiments with precipitated Silica. Average diameter of grains .00040 cm. Estimated area of surface per gramme 6820 sq. cm.

Number of Experiment.	Mass of powder in grammes.	Mass of bulb.	Mass of water, including water-equivalent of calorimeter, powder, bulb, thermometer, and stirrer.	Initial Temp. (Cent.).	Rise of Temperature.	Calories per gramme of powder.	Calories per sq. cm. of surface.
1.	3.940	4.03	207.26	7.320	.136	7.15	.00105
2.	4.282	3.32	190.26	7.300	.164	7.29	.00107
3.	3.760	3.55	201.88	6.930	.134	7.19	.00105
4.	3.602	3.25	195.71	6.238	.132	7.17	.00105
5.	3.721	4.00	196.26	6.770	.136	7.17	.00105
6.	3.601	3.32	211.49	7.200	.122	7.17	.00105
7.	3.256	3.58	205.25	7.106	.114	7.19	.00105
8.	4.166	3.74	214.16	7.502	.138	7.09	.00104
9.	4.261	4.14	197.01	23.636	.164	7.58	.00111
10.	3.950	3.92	182.94	24.180	.162	7.50	.00110
11.	3.657	3.22	202.57	24.410	.138	7.64	.00112
12.	4.789	4.67	206.67	24.000	.178	7.68	.00113
13.	4.417	3.79	212.02	24.060	.160	7.63	.00113
14.	4.691	3.17	230.80	24.670	.154	7.58	.00111
15.	4.003	3.84	227.21	23.906	.130	7.38	.00108
16.	3.829	2.99	227.68	24.700	.124	7.37	.00108

the term $\frac{dh}{dt}$, which appears in the foregoing theoretical investigation. The *same* powder was used throughout, and the results are tabulated in calories per gramme as well as in calories per sq. cm., so that the data should be equally useful whatever be the hypothesis advanced.

The thermometers used in these experiments gave a range of temperature from 5° C. to 25° C.; hence the range over which experiments could be made was rather less than 20° C.

It was found necessary to modify the apparatus so that the calorimeter could be kept for some hours at constant temperature above that of the atmosphere. The cylindrical copper vessel in which the calorimeter was suspended was closed by a tightly fitting copper lid, under the rim of which was tightly packed an indiarubber ring which had previously been stretched around the top of the vessel. Into the copper lid, two copper tubes about two inches long were soldered; through one of these tubes the bulb of the thermometer could be put into the calorimeter, and through the other passed the handle of the crushing instrument. Thus the bulb could be crushed and the liquid stirred and the temperature observed without opening the vessel. The copper vessel was now immersed in several gallons of water, the top of the lid being about an inch below the surface. This water was kept at approximately constant temperature for several hours, during which time the bulb containing the powder was immersed in the water in the calorimeter, so that there could be no doubt about the powder and the water being at the same temperature.

This apparatus proved so satisfactory that it was finally adopted in the later experiments at the lower temperature, instead of the arrangement previously described.

In the first eight experiments the mean temperature was about 7°·1 C. and the mean heat evolved was 7·18 calories per gramme, or ·00105 calorie per sq. cm. In the last eight experiments, the mean temperature was about 24°·3 C. and the mean heat evolved was 7·55 calories per gramme or ·00111 calorie per sq. cm.

$$\text{The mean value of } \frac{dh}{dt} = \frac{\cdot 00006}{17\cdot 2} = \cdot 0000035.$$

$$\text{The mean value of } \frac{h}{\tau} = \frac{\cdot 00108}{288\cdot 7} = \cdot 0000037.$$

Hence, roughly speaking, $\frac{dh}{dt} = \frac{h}{\tau}$ and h varies as τ , that is the heat evolved is roughly proportional to the absolute temperature.

V.

On the Rate of Variation of the Specific Heat of Water with Extension of the Water-Silica Surface.

It has been shown that $\frac{dc}{ds} = \frac{h}{\tau} - \frac{dh}{dt}$, and hence from the results stated above it follows that $\frac{dc}{ds}$ must be very small. If the values of $\frac{dh}{dt}$ and $\frac{h}{\tau}$ are correct to the second significant figure the value of $\frac{dc}{ds}$ is 2×10^{-7} , and this may be taken as indicating the order of magnitude of the term $\frac{dc}{ds}$.

For an accurate determination of $\frac{dc}{ds}$, experiments would have to be made over a much wider range of temperature, and it would be advisable also to obtain, if possible, a silica of much finer and more uniform quality than that used in these experiments.

It is known that the surface-tension of a liquid in contact with air can be represented approximately as a linear function of the temperature, and hence, from equation (vii.), $\frac{dc}{ds}$ is approximately zero. But it cannot be assumed that the surface-pressure of water and silica follows the same law as the surface-tension of a liquid in contact with air.

In making any experiment to determine directly the specific heat of water in contact with silica, we are met at once with the difficulty that the specific heat of silica is not accurately known.

According to Joly * the specific heat of amorphous silica is $\cdot 2375$, but it has been suggested † that this value is too high, and that the error arose through neglect of the Pouillet effect; a similar question in regard to the specific heat of carbon has been investigated by Kopp, Wüllner & Bettendorf, and Weber ‡.

Bellati §, in his attempt to determine the specific heat of moisture absorbed by silica, took for the specific heat of the silica the value $\cdot 1993$ as the mean of the various values obtained for different forms of silica.

The value of $\frac{dc}{ds}$ cannot, however, be obtained by direct

* Joly, Proc. R. Soc. xli. p. 250 (1886).

† Martini, *Atti del R. Istituto Veneto*, Tomo lix., Parte seconda, p. 637.

‡ Weber, *Pogg. Ann.* t. 154, pp. 367-423 (1875).

§ Bellati, *Atti del R. Istituto Veneto*, Tomo lix., Parte seconda, p. 945.

experiments such as those made by Bellati. Suppose, for example, p grammes of silica having a specific heat k , and w grammes of water, are mixed and raised to a temperature t , and the mixture is then put into a Bunsen's ice calorimeter and cooled to 0°C. , the heat given up is

$$\left(pk + w + p \cdot s \cdot \frac{dc}{ds} - p \cdot s \cdot \frac{dh}{dt}\right)t = \left(pk + w - p \cdot s \cdot \frac{h}{\tau}\right) \cdot t,$$

approximately, from equation v.

It is necessary, therefore, to distinguish between the *true* or *absolute* variation and the *apparent* variation in the specific heat of water in contact with a solid. The *true* variation in the specific heat is proportional to $\frac{dc}{ds}$, and is probably very small; but since in any experiment it is impossible to prevent the evolution or absorption of heat at the surface depending on the term $\frac{dh}{dt}$, the *apparent* variation in the specific heat, that is, the variation actually observed in any experiment, is proportional to the difference of the terms $\frac{dc}{ds}$ and $\frac{dh}{dt}$, that is, approximately proportional to $\frac{h}{\tau}$.

Hence the *apparent* specific heat of water in contact with a solid is approximately $\left(1 - \frac{A}{w} \cdot \frac{h}{\tau}\right)$, where A is the area of the surface of the water in contact with the solid, and w the mass of the water. For example, in the earlier experiments of the present investigation, the mass of water was about 200 grammes and the area of surface exposed by 4 grammes of powder was $4 \times 10900 = 43600$ sq. cm., and the value of $\frac{h}{\tau}$ was 37×10^{-7} : hence the *apparent* specific heat of the water was equal to $(1 - \frac{43600}{200} \times 37 \times 10^{-7}) = .99919$. It is evident that if the mass of water is small compared with the mass of powder, the variation in the apparent specific heat may be very great, so that it is not necessary to assume, as Martini did, that some of the water is solidified on the surface of the powder, in order to account for the apparent variation in the specific heat.

VI. *Experiments with Mercury.*

Experiments were made to show a *fall* of temperature on putting a finely divided solid into mercury. After several fruitless attempts with silica, the following method was adopted.

About 3000 grammes of mercury were placed in a glass beaker, and some cotton silicate was placed in the same beaker above the mercury; above the cotton silicate was a cardboard disk which covered the silicate entirely, except that a space was left for the insertion of the thermometer, and a little space was allowed for the edge of the disk to clear the sides of the beaker. On pressing down the disk the cotton silicate was suddenly immersed in the mercury, and in some experiments there was a fall of temperature amounting to $\cdot 016^{\circ}\text{C}$. But the results were not consistent, for in other experiments there was a slight rise of temperature, caused probably by the cotton silicate being at a higher temperature than the mercury. After leaving the cotton silicate immersed in the mercury for some time, so as to take the same temperature, it was suddenly released, and a rise of temperature was the invariable result. With 11 grammes of cotton silicate the rise of temperature was about $\cdot 02^{\circ}\text{C}$., and with 30 grammes of silicate the rise of temperature was about $\cdot 05^{\circ}\text{C}$., but the results varied considerably.

These experiments do not lend themselves to quantitative measurement, for the surface of the mercury cannot be determined. When the filaments of cotton silicate are put into mercury they tend to cling together in bundles or tufts, and the mercury breaks up into a great number of little globules between the tufts of silicate. The surface exposed by the mercury is thus large and indeterminate. The results show, however, that the sudden contraction of a mercury surface causes an evolution of heat and corresponding rise of temperature, and the effect can be regarded as a modification of the Pouillet effect for a liquid which does not *wet*, or enter into intimate contact with the solid.

H.M. Dockyard School, Portsmouth,
March 1902.

XXVIII. *On some of the Consequences of the Emission of Negatively Electrified Corpuscles by Hot Bodies.* By J. J. THOMSON, M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge*.

IT was shown by Elster and Geitel† that an incandescent metal wire in a good vacuum emits negative electricity; in 1899 I showed that the carriers of this negative electricity were “corpuscles,” *i. e.* were identical with the carriers of

* Communicated by the Author.

† Elster and Geitel, Wied. *Ann.* xxxvii. p. 315.