La Mer, Gronwall and Greiff are in somewhat better agreement with the experimental values than the original Debye–Hückel approximation.

STATE COLLEGE, PENNSYLVANIA
RECEIVED MARCH 6, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, PHOENIX PHYSICAL LABORATORIES]

Thermal Effects Produced by the Exposure of Massive Gold to Saturated Water Vapor

BY FREDERICK BARRY AND ELLIOTT PIERCE BARRETT

In 1922, during an investigation of sources of error in precise adiabatic calorimetry carried out in this Laboratory[1] a slow evolution of heat was observed under conditions designed to maintain constant temperature, which, after it had been found to occur only when moisture was present in the insulating air-gap, and to persist after the most careful precautions had been taken to ensure the absence of distillations and chemical changes, was tentatively ascribed to the absorption of water on the external gold-plated surface of the calorimeter. Approximately measured, this effect was found to approach a total development of about 0.035 gram-calorie per sq. cm. of surface, and thus to be large enough to occasion serious errors in precise measurement. Evidently, therefore, it demanded further study, and for more than practical reasons, since its magnitude was quite out of accord with theoretical anticipations if it were to be ascribed to simple adsorption.

The present paper describes the precise measurement of this heat, which, tentatively and for convenience, we shall still call a heat of adsorption, by one of two methods that were found to be practicable for the purpose.

Apparatus and Procedure

A diagrammatic sketch of the apparatus used is shown in Fig. 1. Within a heavy closed jacket of nickel-plated brass (J) a disk of gold (D) was suspended horizontally by a gold wire from a loose button supported near the top of a central chimney. This disk was provided with a small tubular pocket into which there fitted tightly the metal-capped end of a flexible copper–constantan thermel of eight junctions (T), the other end of which was similarly fitted to the jacket wall. The jacket was also provided with an inlet tube (I) by means of which air from a drying chain or water from a reservoir (R) could be delivered to the bottom of the chamber; and with an outlet tube (O) attached to a second chimney that carried the thermel leads, through which air could escape. The jacket, having been completely assembled, was submerged to the indicated level (L) beneath the water of a large bath (B) the temperature of which was kept uniform by a very rapid circulation of its entire mass. This was effected by a powerful propeller (P) which drew the water downward in a uniformly flowing stream around the jacket on the inside of a coaxial baffle (S) and against the hemispherical bottom (C) which re-directed it upward on the outside of the baffle without turbulence. The baffle itself,

---

[1] THIS JOURNAL, **44**, 899, especially 931–934 (1922).

made of sheet copper and nickel-plated, not only guided the flow of water but also protected the jacket against radiation from the bath-heater (H). By means of this heater, which functioned continuously during measurement, the temperature of the bath could be kept constant under the control of a thermoregulator (TR) or, without this control, could be made to rise at a rate a little greater than that which was necessary to keep the system adiabatic during the period of most rapid adsorption. In this and subsequent times any desired smaller change of temperature in the bath could be established by the manual control of a stream of cold water delivered from a reservoir of constant level placed above the bath where it was held at fairly constant temperature. This stream flowed through a needle valve in the delivery pipe (W) the adjustment of which was made very precise by means of a long handle attached to its head, the exact rotation of which was shown by a pointer which, when the valve was turned, swung over a graduated circle 25 cm. in diameter. The bath temperature was indicated by a mercury thermometer (M); and with reference to this, that of the suspended gold disk was determined by the thermel (T). The whole system above the bath level was enclosed in an adjustable air thermostat essentially similar to that used by Smith in a preceding research, and similarly controlled.[2]

The bath stirring in this system was more effective than any yet tested in this Laboratory. When the jacket was protected by the baffle against radiation from the bath heater it ensured a uniformity of temperature about the jacket precise within 0.001 °. The mercury thermometer had been standardized to $\pm 0.0002°$ at $0.01°$ intervals by an electrical method elsewhere described.[3] It was remarkably free from capillary friction, was very easily read with a telescope to the nearest millidegree, and responded to temperature changes of this magnitude within fifteen seconds. The thermel was standardized by comparison with this instrument and was comparably precise: with the galvanometer assemblage used it indicated 6.0 millimeters of scale per millidegree thermal head between its junctions.

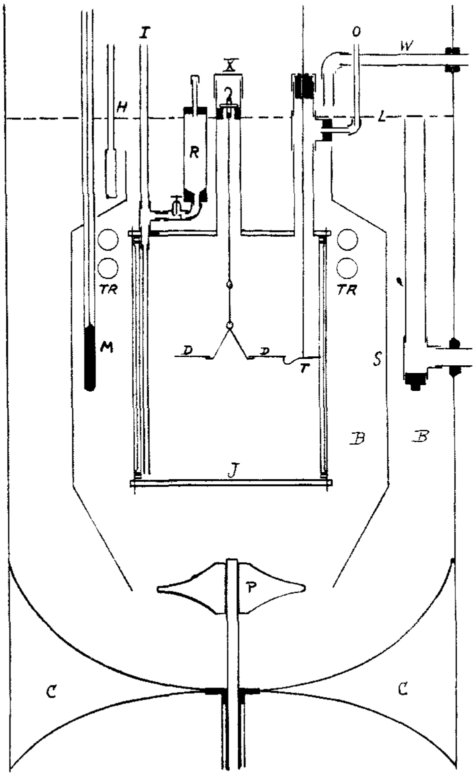

Fig. 1.

Thermal Measurements

Maintenance of Adiabaticity.—In this system there was inevitable thermal stratification, as a consequence of which it could not safely be assumed that, when the temperature readings of the disk and bath were the same, a condition of compensating

---

[2] Barry and Smith, THIS JOURNAL, **55**, 2215 (1933).

[3] Barry, Webb and Smith, *ibid.*, **54**, 3785 (1932).

leakages obtained which would be equivalent to adiabaticity. To discover the galvanometer deflection which indicated this condition in the saturated system, the calorimeter was assembled and, after 50 cc. of water had been introduced from the reservoir, was allowed to stand under thermostatic control for two days before observations were made, in order that the process of adsorption on the disk and jacket wall, which was known to be very protracted, should be brought to full completion. The thermel then indicated that the temperature head of the bath with reference to the disk was −0.002°; and afterward, when the system was taken under a more exact manual control, it was found that so long as this indicated negative head was maintained no change of temperature was observed. Repeated tests of the efficacy of the same control during many hours' maintenance, also, never showed any change in temperature as great as ±0.001° in periods of half an hour. It was thus indicated that error of measurement due to imperfect manipulation would be negligible, since even a persistent drift of 0.002° an hour—the most unfavorable presumption possible—would produce a change of only 0.0140° in seven hours, which was the duration of the longest measurement made; and this is within the limit of other experimental errors, as will be shown later. It will be noted that a temperature change of ±0.001° in this system corresponds to a gain or loss of only ±0.006 calorie of heat (p. 3093) and 0.0140°, therefore, to less than 0.1 calorie.

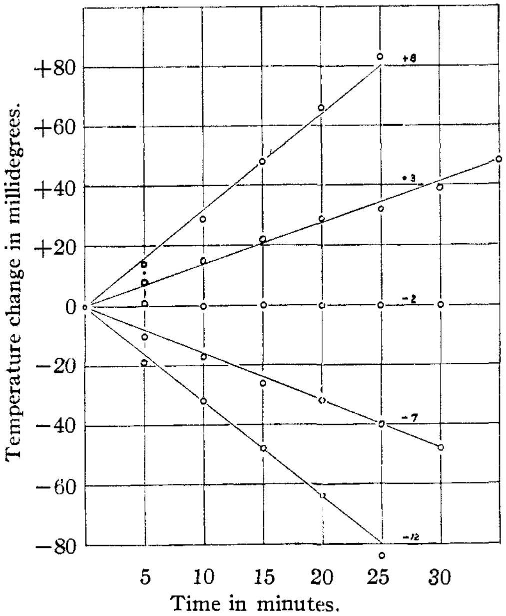

Fig. 2.—Thermal leakage of the adsorption calorimeter.

Investigation of Thermal Leakage.—The condition of practical adiabaticity having been thus determined, measurements of leakage were made under thermal heads which were symmetrical about the indicated bath head of −0.002°. The results of these measurements were fully confirmatory, for, as is shown in Fig. 2, the leakages for bath heads of +0.003 and −0.007 and of +0.008 and −0.012 were almost perfectly symmetrical. The value of the leakage modulus, calculated from these data, was 0.3; that is, the temperature change produced in one minute by a thermal head differing from −0.002° by 0.001° was 0.0003°. This is approximately one hundred times as great as the leakage of similar water-filled calorimeters,[4] and might on casual observation have been taken to mean that an adequate control of the system was impossible, had it not been for the evidence provided by the symmetrical distribution of leakages about the indicated head of −0.002°, and for the fact that a return to this indicated head always resulted in the establishment of the isothermal condition.[5]

---

[4] THIS JOURNAL, **44**, 918 ff. (1922).

[5] During a measurement there was at all times a layer of water about 1 mm. deep over the bottom of the jacket. If then the environmental temperature rose slightly, the vapor pressure of water in the system would increase and water would distil from the warmer jacket to the colder disk. If the en-

Procedure.—The procedure in measurement was as follows. The disk being suspended and the thermel being in place, the jacket was assembled dry as the laboratory air was dry. It was then placed in the bath and 50 cc. of distilled water was pipetted into the reservoir. The water-bath and air chamber were then placed under thermostatic control and air was drawn through the jacket from a drying chain. When the drying had been continued for the desired length of time, the needle valves of the inlet and outlet tubes were closed. The bath was then taken under manual control, and was cooled until the thermel showed the previously determined equilibrium gradient of −0.002° bath head. The drying was then discontinued, the bath temperature was adjusted, and ten minutes later the reaction was initiated. By this procedure the thermal effect of a slight initial leakage, which was definitely traced to the diffusion of water vapor through the rubber gaskets of the jacket and which (it is important to note) introduced an error of *defect* into the final results of measurement, was kept below significant magnitude. Within fifteen seconds after the introduction of the water into the jacket the temperature of the disk began to rise rapidly. The bath temperature was adjusted in accordance with the thermel deflection as previously described, and the reaction was followed in this way as long as was desired. The bath temperature was read just before introducing the water, at five-minute intervals during the first half hour, and thereafter every fifteen minutes. The time–temperature curves obtained in this way were smooth to ±0.002° in every measurement.

Measurement.—Two causes of variability in the results of the first measurements thus made, neither of them due to inadequate calorimetric technique, were with great difficulty overcome. The first of these was quickly traceable to chemical contamination of the disk by its initial cleaning with chromic and sulfuric acids; and in consideration of the care that had been taken after cleaning by protracted drenching and soaking in water to rid its surface of adhering contamination, seemed explicable only upon the assumption that the cleaning agents had penetrated the metal either by capillary imbibition or by occlusion—a supposition consistent with the subsequent persistence and very slow diminution of its effect after repeated steamings of hours duration. The final elimination of this source of error, however, was assumed to have been accomplished when, after twenty-eight measurements had been made, each preceded by prolonged steaming and soaking of the disk, no further diminution of the thermal effect of the adsorption was detectable.

The second of these causes of variability had smaller but more irregular effects; and seemed to be due to dissimilar initial conditions of measurement, occasioned by varying incompleteness of the preliminary drying. It was at length reduced to negligible magnitude by slowly blowing the air with which all inner jacket surfaces were finally dried over solid drying agents only, before the jacket was immersed; and by exercising particular care in protecting the outlet by tubes filled with adequate quantities of the same desiccants. In the drying train finally used the ultimate element was a tube 3 cm. in diameter and 80 cm. long filled with beads that carried phosphorus pentoxide,

---

vironmental temperature fell slightly below the equilibrium value, water would distil from the disk to the jacket wall. These distillations easily account for the excessive leakage observed; and the experimental fact that, in the absence of superimposed effects, such a system can be kept isothermal, is a very remarkable indication of the efficacy of thermoelectric control in calorimetry. The success of the procedure undoubtedly was due to the circumstance that the actual fluctuations in bath temperature were minute. The maximum fluctuation during the major part of any measurement was ±0.0005°, and the average fluctuation was ±0.0003°.

It will be shown later (page 3094 and Fig. 4), in connection with the gravimetric investigation, not only that the distillations above referred to occurred but also that their magnitude was observed, and that distillations due to fluctuations of the order of ±0.0005° were entirely negligible.

A calorimetric system thus kept in a condition equivalent to adiabaticity by a compensation of leakages may, for the sake of brevity and consistently with analogous terminology, be called a *metadiabatic* system.

which received air already dried by 140 cm. of calcium chloride in a similar tube; and through this the air was blown at the rate of 300 cc. a minute for twenty hours or more, at which rate the total volume that passed through the system was fifty-five times its capacity. Twenty hours of such drying was sufficient to bring a phosphorus pentoxide tube at the outlet to constant weight; and the results of the last measurements of the heat of adsorption, which were preceded by periods of drying of 22.5, 70 and 46 hours, respectively, yielded results consistent to 0.001 calorie (which at the initial rate of adsorption corresponds to 0.00008 g. of condensed vapor) and not in the corresponding inverse order of magnitude. It was thus made evident that in these measurements the initial concentration of water vapor in the jacket was, within the limit of error of the calorimetry, the same and probably very near to that corresponding to the vapor pressure of phosphorus pentoxide.

The Time–Heat Curve.—A simple mathematical expression describes the liberation of heat with time, to well within the limits of experimental error. The heat already evolved at any time can be expressed by the exponential function

$$H = e(a - b/t^c)$$

where H is the heat in millicalories per square centimeter, t is the time, and a, b and c are arbitrary constants. Table I shows the mean values of determinations No. 32 and No. 33 as obtained by observation and by calculation from the equation

$$\log_{10} H = 1.5990 - (0.3486/t^{0.4090})$$

Logarithms to the base 10 were used as a matter of convenience and the constants were evaluated by using the observed values of the heat at 1, 2 and 4 hours. Table I includes the values of the actual temperature changes observed, as well as the quantities of heat to which they correspond, in order to show more vividly the fact that the use of the low heat capacity system chosen for the work permitted the magnification of these relatively small

TABLE I

COMPARISON BETWEEN THE OBSERVED VELOCITY OF THE THERMAL EFFECT PRODUCED BY THE EXPOSURE OF MASSIVE GOLD TO WATER VAPOR AND THE VELOCITY CALCULATED FROM THE EMPIRICAL EQUATION LOG H = 1.5990 − $(0.3486/t^{0.4090})$

Time, hours	Change in temp. in millidegrees Det. 32	Det. 33	Corresponding heat in millicalories per sq. cm. Mean obs.	Mean calcd.	Time, hours	Change in temp. in millidegrees Det. 32	Det. 33	Corresponding heat in millicalories per sq. cm. Mean obs.	Mean calcd.
0.0	0	0	0.0	0.0	5.0	850	893	26.1	26.2
.25	293[a]	330[a]	9.4		5.5	863	904	26.5	26.6
.5	422	468	13.3	13.7	6.0	873	914	26.7	27.0
1.0	578	610	17.8	(17.8)	6.5	883	925	27.1	27.3
1.5	653	690	20.0	20.1	7.0	892	933	27.3	27.6
2.0	707	743	21.7	(21.7)	10				29.1
2.5	743	785	22.8	22.9	100				35.1
3.0	775	816	23.8	23.5	1000				37.9
3.5	799	838	24.5	24.6	Infinity				39.7
4.0	818	862	25.2	(25.2)					
4.5	835	881	25.7	25.7					

[a] Corresponding readings made at each subsequent quarter hour are here omitted.

thermal effects to such an extent that slight errors of control could not possibly leave the results seriously in doubt.

Measurement of Heat Capacity.—The data of Table II involve the acceptance of the value 6.4 gram calorie units for the heat capacity of the system. This heat capacity included, beside that of the disk—which could be closely enough estimated from its weight and specific heat—that of unknown parts of the surrounding air, the thermel, and the suspending wires. Since the heat capacity of the disk alone was only 6.2 gram-calorie units and that of all the air in the jacket was about 1.5 such units, it was necessary to know at least what fraction of the latter to include in the effective heat capacity. This could be determined only by direct measurement.

To make this measurement, an auxiliary gold-plated copper disk was used which held an insulated manganin resistance wire imbedded in a low-melting alloy. With this disk the system was assembled and was prepared for measurement and subsequently controlled precisely as in a measurement of adsorption. An adiabatic condition having been established and the constant initial temperature read, a steady electrical current, under a measured potential so adjusted that the rate of temperature change was closely the same as the mean rate in an adsorption, was switched through the disk coil at a determined time. After the temperature had risen about a tenth of a degree, it was switched off at a second determined time; and when an isothermal condition was again established the final temperature was read. The resistance of the disk-coil having been determined, the data so obtained yielded the total heat capacity of the system, the heat capacity of the accessory disk, alone, having been estimated from the weights and specific heats of its parts. The determined total heat capacity of the auxiliary coil system was 15.8, that of the auxiliary coil alone 15.6, and that of the gold disk 6.2 gram-calorie units. The effective heat capacity of the adsorption system, determined by ten measurements which showed a mean deviation from the mean of 0.14 gram-calorie units, was 6.4 gram-calorie units, precise within ±0.2 such units, or to within 5%.

Since the thermometric error in any one of the determinations of adsorption heat cannot have exceeded ±0.001° (p. 3089) which corresponds to ±0.00003 cal. per sq. cm., and since the maximum error due to inadequate maintenance of practical adiabaticity was 0.014° in seven hours (p. 3090) which corresponds to ±0.0004 cal. per sq. cm., it is clear that the error in this determination of heat capacity may be taken to define the reliability of the whole thermal investigation. Indeed, the mean discrepancy between the results of the final measurements of adsorption heat is of about the same magnitude (Table I).

Gravimetric Measurements.—The total heat of adsorption and its rate of development in time having been measured, the relation of this heat to the actual mass of vapor adsorbed was then determined by carrying out a measurement wholly similar to the preceding, during which, however, the disk was suspended from the pan of a sensitive balance and its change in mass observed as adsorption occurred.

The weighings were made with an analytical balance, sensitive to ±0.1 mg. when laden with the disk, very carefully installed in such wise that while it operated thermal leakage from the system was minimal, and adequately tested at convenient intervals for consistency of behavior. The first weighing was made fifteen minutes after water had been introduced into the thoroughly dry system, and thereafter at intervals of fifteen minutes. Throughout the determination the bath temperature was adjusted in accordance with the indications of a time–temperature curve which represented the mean result of the final determinations 32 and 33 (Table II) drawn on a scale large enough to be read easily to one millidegree.

In regulating the bath temperature the operator endeavored to guess at the correct adjustment which would produce a linear rise that approximated the rise indicated by the curve during the given time interval. If the guess was wrong the adjustment was not changed, but its effect was compensated as closely as possible on the next adjustment. This procedure yielded a time–temperature curve which consisted of a series of straight lines joining the points at which a change in adjustment was made, from which the true temperature of the bath at any time could be read directly with slight error.

Results.—The results are shown in Fig. 3 and in Table II. The figure is of particular interest because it provides direct evidence of the distillations due to irregularities of temperature control to which reference has been made (page 3091). Here the upper smooth curve is the mean time–temperature curve of Determinations 32 and 33: the series of straight lines which vary around it indicate the temperature adjustments made during the gravimetric determination. The lower curve is the best smoothing out that can be made of the broken curve shown superposed upon it, which was obtained by straight line interpolation between points determined by momentary observations of increasing weight. It will be noticed that whenever an adjustment caused the bath temperature to rise too rapidly, then the weight increased rapidly, that when the adjustment produced too slow a rise in bath temperature, then the weight decreased, and that when the adjustment more closely approximated the continuous rise of temperature indicated by the predetermined curve, the weight showed a small but regularly definite increment with time. It was inferred from these data that water may be distilled onto the disk by heating the environment, and that it will be distilled off again upon subsequent cooling of the same amount for the same time. It is necessary to show that this compensation is exact within the limits of measurement error. This will be done in the discussion of errors.

The Weight–Time Curve.—Since the heat–time curve was exponential, it was anticipated that the increase in weight with time could be expressed by an analogous equation. This was found to be the case.

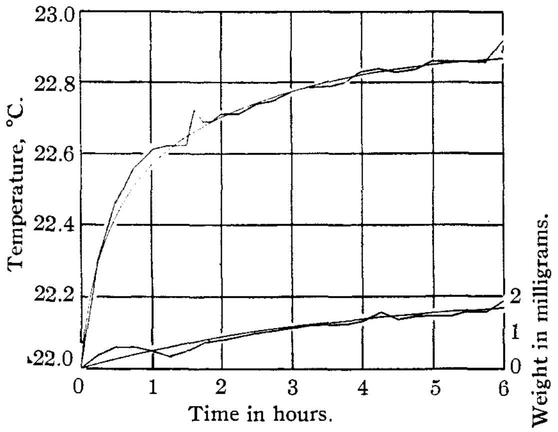

Fig. 3.—Increase in weight during the adsorption of water by massive gold and adjustment of bath temperature during the process.

Table III exhibits the values obtained by drawing a smooth curve through the observed points and through those corresponding on a curve calculated from the equation

$$\log W = 1.724 - (1.025/t^{0.412})$$

in which logarithms are to the base 10, time is expressed in hours, and the weight in grams times 10^4.

TABLE II

COMPARISON BETWEEN THE OBSERVED RATE OF ADSORPTION OF WATER VAPOR BY MASSIVE GOLD AND THE RATE CALCULATED FROM THE EMPIRICAL EQUATION LOG $W = 1.724 - (1.025/t^{0.412})$

Time, hours	Total weight (in grams $\times 10^4$) Obs.	Calcd.	Wt. per sq. cm. (in grams $\times 10^6$)
0.0	0.0	0.0	0.00
.5	2.9	2.3	1.08
1.0	5.0	(5.0)[a]	2.34
1.5	7.2	7.1	3.32
2.0	9.0	(9.0)[a]	4.21
2.5	10.5	10.4	4.86
3.0	11.9	11.8	5.51
3.5	13.0	12.9	6.03
4.0	14.0	(14.0)[a]	6.54
4.5	15.0	14.8	6.92
5.0	15.8	15.5	7.25
5.5	16.3	16.2	7.57
6.0	17.0	17.0	7.95
10.0		20.9	9.77
25.0		28.2	13.18
50.0		32.4	15.14
100.0		37.2	17.40
1000.0		45.7	21.56
Infinity		53.0	24.76

[a] The numbers in parentheses were used to evaluate the constants in the equation $\log W = 1.724 - (1.025/t^{0.412})$.

Errors.—The weighing error was almost certainly less than ±0.1 mg.; for the results of auxiliary tests made under precisely similar conditions when the saturated system was under thermostatic control were concordant to ±0.05 mg. More important, apparently, was the possible error of adiabatic control since this produced distillations between the disk and the jacket. In the manual adjustments of bath temperature, however, it had been attempted to make the thermal effects of these compensatory, and subsequent tests showed that the procedure was effective, to the point of rendering this source of error, in relation to the weighing error, quite negligible.

The saturated system having been in equilibrium under thermostatic control and the disk constant in weight for several hours, the bath was raised a degree above the initial temperature, allowed to cool a degree below it, and then brought back to its original condition. Care was taken to make the rates of rising and falling temperature at the calorimeter surface as nearly equal as possible and so to regulate the cycle as to make the entire change require about an hour to reach completion. Two such tests were made but in reverse order; that is, in the first test the bath was heated, cooled and heated; and in the second it was cooled, heated and cooled. Weighings made upon completing these cycles showed that the disk retained about one milligram of water vapor at the end of the cycle in both cases, and that this excess did not disappear for many hours. It was clear that this lag was a source of error in measurement; but evaluation proved that its effect was negligible. In the gravimetric measurement the maximum cycle passed through was less than ±0.05° in an hour, which—if the distillation were proportional to time and, for such small differences of temperature, to thermal heat—would result in an excess of weight not greater than 0.05 mg., which is less than the estimated error of measurement. In the thermal measurements the maximum cycle passed through was not greater than ±0.0005° in five minutes, which would produce an increment of weight not greater than 0.00025 mg., which is altogether negligible.

The Molal Heat of Adsorption.—It has been shown (pp. 3092 and 3095) that both the thermal increment with time and the increment of adsorbed vapor with time can be expressed by an equation of the form $Y = e^{(a - (b/x^c))}$. It is therefore possible to express the ratio of heat liberated to weight adsorbed during any given time interval. This has been done, and the results are shown in Table III.

TABLE III

RATIO OF HEAT LIBERATED TO WEIGHT OF WATER VAPOR ADSORBED DURING SUCCESSIVE TIME INTERVALS AFTER EXPOSING MASSIVE GOLD TO SATURATED WATER VAPOR

Time intervals in hours	Thermal increment in millicalories per sq. cm.	Weight increment in grams $\times 10^6$ per sq. cm.	Ratio of heat to weight in cal. per g.
0–1	17.8	2.35	7570
1–2	3.9	1.90	2050
2–3	1.8	1.30	1380
3–4	1.7	1.00	1700
4–5	1.0	0.75	1330
5–6	0.8	0.70	1140
(6–10)[a]	(2.1)	(1.85)	(1130)
(10–100)	(6.0)	(7.60)	(790)
(100–1000)	(2.8)	(4.20)	(670)
(1000–Infinity)	(1.8)	(3.20)	(560)

[a] Values in parentheses extrapolated.

The limiting value of the ratio as the process approaches completion could have been predicted; for, since at all times this system contains liquid water, the reaction must proceed until the vapor pressure of water from the gold is equal to that of free water. This is equivalent to saying that the value of the ratio of heat increment to weight increment, as the reaction approaches completion, must approach the heat of evaporation of water as a limit. The ratio of heat increment to weight increment from 1000 hours to infinite time can be regarded without serious error as representing the limiting value of the ratio. The value obtained from the equations by extrapolation, namely, 560 calories per gram, checks the accepted value of 582 calories per gram to within the limits of measurement error.[6] Table III may therefore be regarded as a check upon the whole investigation; for it seems highly improbable that the agreement could be fortuitous.

The results of Table III, it will be noted, fully confirm the partial and much less precise results formerly obtained.[1] As against the original approximate value for the heat of adsorption of water vapor on gold of 0.035 gram calories per sq. cm. of surface, the summation of the second column of Table III yields the corresponding value 0.040. This correspondence indicates clearly that the phenomenon is of the same general character on plated surfaces and on massive metal. It is worth noting also that the preliminary measurements of the present research, made in another way with a newly plated surface, and subsequent trial measurements conducted by the method here described but with a different disk, gave satisfactorily comparable results.

Summary

1. A calorimetric method has been devised which permits the measurement, to within ±0.0005 gram calorie, of heats produced by the exposure of metals to vapors.
2. By this method the heat liberated on the exposure of massive gold to water vapor in equilibrium with liquid water and its rate of development during seven hours at 22–23° have been measured. This heat is evolved exponentially. In seven hours it is 0.0276 cal. per sq. cm. of surface; extrapolated to infinite time it is 0.0397 cal. per sq. cm.
3. The quantity of water adsorbed during this thermal change has been determined by direct weighing, and found to be after six hours 7.95×10^{-6} g. per sq. cm., and after infinite time 24.76×10^{-6} g. per sq. cm. Its rate of deposition is exponential; whence it is calculated that the heat developed in the process gradually diminishes from an initial value of 7570 cal. per g. to a final value that approximates the heat of vaporization of water, namely, 560 cal. per g.; the total heat evolved being 1601 cal. per g.

---

(6) The value 582.3 at 25° given in the Landolt-Börnstein tables was determined by Smith in 1907 by a method entirely free from errors due to adsorption.

4. These results substantially confirm the observations previously made in this Laboratory [Barry, THIS JOURNAL, **44,** 933 (1922)] which yielded the approximate value for the total heat similarly developed on a gold-plated surface of 0.035 cal. per sq. cm.

5. The phenomenon, which is certainly not an adsorption in the usual sense of the term, awaits full explanation. It appears to involve the occlusion of water vapor by gold, and to be affected, at least, by capillary imbibition.

NEW YORK CITY

RECEIVED MARCH 11, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Thermal Decomposition of Methyl Azide. A Homogeneous Unimolecular Reaction

BY JOHN A. LEERMAKERS[1]

The author has recently studied the thermal decomposition of ethyl azide[2] and has found it to be a homogeneous, unimolecular reaction. It seemed advantageous to study the next lower homolog in the series of azides, methyl azide. Ramsperger[3] made some preliminary experiments on the decomposition of methyl azide and reported that it was homogeneous and unimolecular. He did not find it feasible to continue the investigation over a range of temperatures and pressures because of his experimental method. His work was confined to five experiments at 245° at initial pressures from 5.7 to 0.05 cm. The present investigation was conducted over the temperature range 200–240° and from initial pressures of 46.6 to 0.078 cm.

Nature of the Reaction.—When methyl azide decomposes at constant volume and constant temperature the final pressure is 1.66 times the initial pressure. This ratio is independent of temperature and pressure. Ramsperger reported that in his experiments the ratio was 1.55. It was found in the present investigation that the ratio for the first several experiments was 1.54 but that after these experiments it was 1.66, where it remained practically constant. In the last experiments performed the ratio slightly increased to 1.68.

In order to determine the products of the reaction, freezing out experiments were made after complete decomposition of methyl azide at 240°. The procedure was exactly as described in the previous work on ethyl azide.[2] The results are given in Table I. Pressures have been corrected for the volume of the tube immersed in the cold baths.

---

[1] National Research Fellow in Chemistry.

[2] Leermakers, THIS JOURNAL, **55,** 2719 (1933).

[3] Ramsperger, *ibid.*, **51,** 2134 (1929).