348. *The Thermocouple Vacuum Calorimeter.*

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The experimental measurement of heats of adsorption is of importance for the study of heterogeneous catalysis, especially in cases where on account of difficulty in reaching equilibrium, the thermodynamic method cannot be applied. For this purpose, the thermocouple calorimeter appears to offer the most promise since it can be used over a range of temperatures, and might be employed at those temperatures at which catalytic processes are usually carried out. There are, however, many difficulties to be overcome before this calorimeter can become an accurate instrument for research purposes. Up to the present, the design of such calorimeters has not been entirely satisfactory even for work at room temperatures. The main difficulty is to ensure that the temperature recorded by the thermocouple is a true measure of the rise in temperature of the mass of the adsorbent. Temperature gradients are set up across the adsorbent during the adsorption which can be ascribed to the operation of three main causes: (1) the loss of heat from the external surface of the calorimeter, (2) a slow rate of distribution of the liberated energy to the various parts of the calorimeter, and (3) an unequal distribution of the adsorbed gas throughout the catalyst. In the design of a vacuum calorimeter it is necessary to pay attention to each of these causes of temperature gradients. Perhaps the most important condition for the satisfactory working of a calorimeter is that the rate of loss of heat from the external surface should be small relatively to the rate at which heat is distributed within the calorimeter.

There are two main types of thermocouple calorimeters in use, *viz.*, (1) that devised by Garner, Bull, and Hall (J., 1931, 837), which consists of a cylindrical platinum vessel with a gauze tube along its axis, the adsorbent being placed in the annular space formed by the cylinder and the gauze tube and the gas being admitted to the space *outside* the radiating surface, and (2) that employed by H. S. Taylor and his co-workers in which the adsorbent is placed in a glass vessel which is surrounded by a hard vacuum during the measurement of the heat of adsorption and the gas is admitted to the inside of the radiating surface.* The former gave results in the adsorption of oxygen on charcoal which were in satisfactory agreement with those obtained by Marshall and Cook (*J. Amer. Chem. Soc.*, 1929, **51**, 2019) with an ice calorimeter and by Lendle (*Z. physikal. Chem.*, 1935, *A*, **172**, 77) in a multiple thermocouple calorimeter. The adsorption of small volumes of oxygen on charcoal is, however, exceptional, in that the adsorption process is so complete that a high vacuum is obtained within a few seconds after the admission of gas. The Newton coefficient for the calorimeter is therefore constant throughout the measurements. It would be otherwise if the adsorption process were slow, for in such a case the pressure falls continuously during the adsorption. On account of the difficulty in interpreting the results for slow processes, the second type of calorimeter, where a hard vacuum is maintained outside the radiating surface, would seem to have most promise for general work. Consequently, in this investigation, attention has in the main been directed to this type of calorimeter.

The rates of loss of heat from the radiating surface of various forms of calorimeter have been investigated under conditions such that the pressure of the gas over the adsorbent could be varied. Zinc oxide–chromium sesquioxide in granular form was employed as an adsorbent in most cases, since this substance gives rise to a great variety of adsorption processes. A type I calorimeter (Fig. 1*a*) gave cooling coefficients which decreased with fall in pressure (Fig. 2*a*).† This was compared with a calorimeter consisting of a very thin cylindrical bulb of Pyrex glass (Fig. 1*b*) with an inlet tube of very thin glass 0·7 cm. in diameter, and it was found that, in this case also, the Newton coefficients varied with the pressure (Fig. 2*b*). This was shown not to be due to loss of heat *via* the inlet tube by reducing its diameter to 2 mm. (Figs. 1*c* and 2*c*). In order to determine the cause of the vari-

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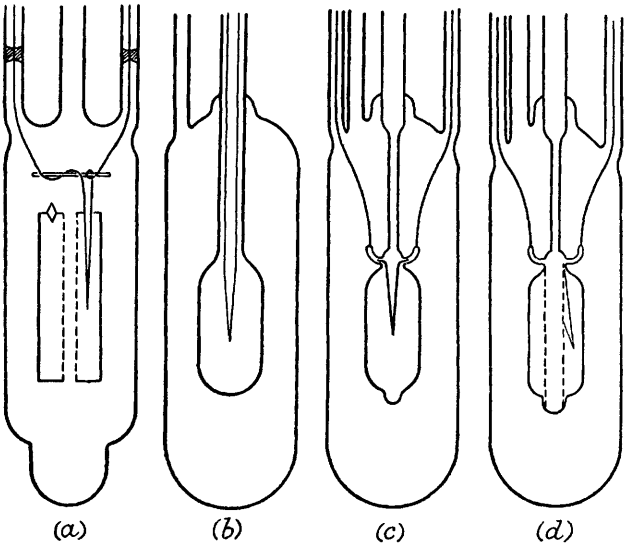
* The calorimeter employed by Ward (*Proc. Roy. Soc.*, 1931, *A*, **133**, 506) may be classed as of this type, although his calorimeter was surrounded by air.

† The cooling coefficients are expressed as loss of temperature in degrees per minute for a temperature difference of 1°.

ation in the loss of heat with the pressure of gas over the adsorbent, measurements were made of the heat of adsorption of hydrogen on the same catalyst, in the calorimeter 1*d*, which gives a similar change in the Newton coefficient to 1*c*.

Heat of Adsorption of Hydrogen on Zinc–Chromium Catalyst in Calorimeter 1d.—The calorimeter was tested by non-adiabatic and adiabatic methods. The rise in temperature as shown by the thermocouple was recorded photographically, and measurements were made simultaneously of the gas pressure above the adsorbent. In evaluating the heat of adsorption, corrections were applied for the variation in the Newton coefficient with pressure. In the non-adiabatic method, the external temperature was maintained at the initial temperature of the calorimeter throughout the experiment. In the adiabatic method, hydrochloric acid was run into a dilute solution of sodium hydroxide which served as the calorimetric fluid, and the rate of introduction was so adjusted as to keep the temperature of the surrounding medium at that shown by the thermocouple. Some experiments were also carried out during which the external temperature was maintained approximately at that of the maximum temperature reached during the adsorption. This will be referred to as the partial adiabatic method.

FIG. 1.



There was, in general, a slight fall in the heat of adsorption with successive admissions of gas, but the differences were so slight that the average results of the first three admissions can be given: non-adiabatic method 21·1; adiabatic method, 19·0; partial adiabatic method 18·7 cals./mol. The lack of agreement shows that calorimeter 1*d* is unreliable, and this was to be expected since the cooling correction after 4—5 minutes is 30% of the rise in temperature. With a correction of this magnitude, it seemed probable that there were large temperature gradients across the calorimeter, so calculations were made of the rates of transference of heat across various parts of the calorimeter in order to test this view.

Conduction of heat along the thermocouple wires. The thermocouple was platinum–platinum-rhodium of 46 gauge, and the length of the wires was about 12 cm. before they ended in a heat sink. It can easily be shown that the fall in temperature of the calorimeter is $1{\cdot}9 \times 10^{-5\circ}$/min. for 1° difference in temperature, which is a negligible contribution to the total loss, *viz.*, 0·03—0·08°/min.

Conduction of heat along the exit tube. Likewise, it can be shown that the rate of loss of heat along the exit tube is $0{\cdot}005x^\circ$/min., where x is the cross-sectional area of the glass. Since x is a small fraction of 1 cm.^{2}, it is clear that loss by this means is also negligible, and that practically the whole of the heat loss is by radiation from the surface of the calorimeter.

Loss by radiation. The container of the calorimeter consists of a cylindrical bulb 7·3 cm. long and 2·75 cm. in diameter with hemispherical ends, and, the emissivity of Pyrex glass being taken as 0·9 at 20°, it can be shown that the loss of heat by radiation from the walls for 1° difference in temperature is 0·225°/min. These calculated losses are 3—10 times as large as those measured experimentally, so the actual temperature of the radiating surface must be much lower than the temperature of the interior as shown by the thermocouple. There are, therefore, very large gradients across the calorimeter. In order to gain some idea of the locality of these gradients, calculations were made of the rate at which heat is transmitted across the glass wall of the calorimeter and the jacketing vessel.

Gradients across Pyrex walls. Ingersoll and Zöbel ("Theory of Heat Conductivity," 1913, p. 89) discuss the rate of transference of heat across a slab at uniform temperature, one face of which is raised to θ° and kept at constant temperature, and the other protected from heat loss. From their equations, it can be shown that the temperature of the two surfaces of a slab of Pyrex 0·3 cm. thick becomes the same within 0·5% in about 9 secs. Since the thickness of the outer vessel is 0·3 cm., and that of the thin bulb is very much less than this, it is clear that the lags due to poor conductivity of the Pyrex walls are negligibly small in calorimeter 1*d*.

The transmission of heat across the catalyst, and the thermocouple galvanometer lag. In working with a zinc oxide catalyst in calorimeter 1*f* (see later), information was gained accidentally as to the transmission of heat across the adsorbent and to the thermocouple. It is given at this stage in order that the behaviour of the calorimeter can be adequately discussed. The specimen of zinc oxide adsorbed carbon monoxide and dioxide very rapidly, and the adsorption was complete in a few seconds, although there was a high final gas pressure above the adsorbent. A sharp peak is observed on the temperature–time curves, which was usually 2·5—3 times as high as the one-minute reading (Fig. 6). The duration of the peak was about 30 secs. after the admission of gas. The effect was not observed until the catalyst had been baked out several times, was present only to a slight extent on a second admission of gas, and did not occur on desorption; moreover, it did not occur with ethylene, where a rapid adsorption was followed by a slow process.

The peak on the temperature–time curves can be explained as follows. The granules of zinc oxide are crystalline with very fine cracks, and the activation energy for the surface flow of carbon monoxide and dioxide is so large that the rate of diffusion into the interior along the cracks is negligible. The heat is thus liberated on the outside of the grains, and the thermocouple takes up a higher temperature than is obtained when the heat has become uniformly distributed throughout the grains. The adjustment of the temperature requires about 30 secs., and this is the time taken to equalise the temperature throughout a single grain. It is suggested that the conductivity of heat into the interior of the grains is enormously accelerated if gas is present in the cracks. This accounts for the non-appearance of the peak until the adsorbent has been thoroughly baked out, its non-appearance on second admission, on desorption, and on the adsorption of ethylene.

The peak is of importance because it gives us information as to the rate at which heat is conducted into the interior of the grains when there is a low gas pressure inside the grains, and also indicates the maximum lag on the thermocouple–galvanometer system which is of the order of 30 secs. The losses by radiation during this interval will be small, and there can be no serious objection to the calorimeter on this account.

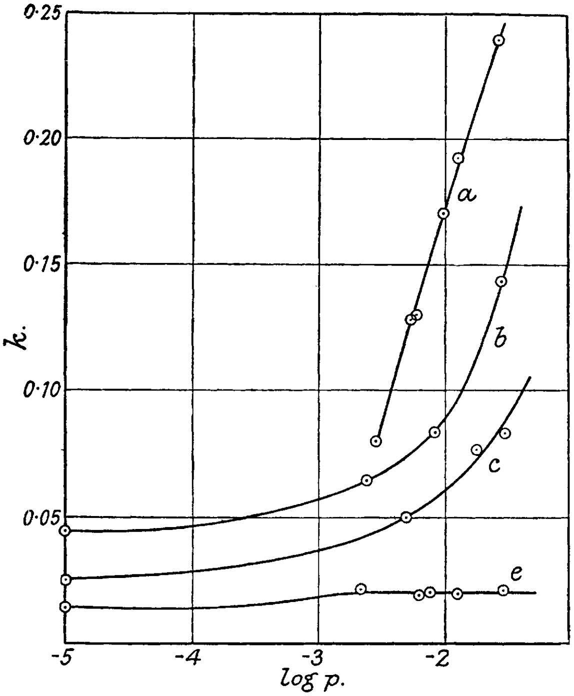
The rate of conduction of heat from grain to grain is a fairly slow process even with gas pressures above 5×10^{-3} cm., and the calculated heats of adsorption do not reach a maximum in the case of hydrogen on zinc oxide–chromium oxide until after about 3 mins. A typical calculation is given below for calorimeter 1*e*.

Time, mins.	2	3	4	5	6	7	8
Heat, cals./mol.	11·9	12·6	12·6	12·7	12·8	12·8	12·7

The lag in the attainment of equilibrium, which is not serious, is due to the time taken for the glass, and the platinum to a less extent, to take up the temperature of the adsorbent.

Calorimeter 1e.—From what has been said above, it will be seen that the improvement of the calorimeter can best be effected by reducing the emissivity of the Pyrex walls. This was effected by platinising the surfaces of the thin bulb and the inner surface of the outer container; this reduced the Newton coefficient considerably, and made it only slightly dependent on the pressure of the gas (hydrogen) in the calorimeter (Fig. 2*e*). When carbon monoxide was employed, a very similar curve was obtained, but helium behaved anomalously (see later). Over the pressure range 5×10^{-3} and upwards, the radiation losses are independent of the gas pressure, and this means that the *gradients across the adsorbent are very slight in this region of pressures.* The cooling correction has also been very much reduced, being only 4% of the rise in temperature after 4 mins. It follows that the irregularities in the temperature of the adsorbent due to conduction into the grains and across the grains to the glass and platinum which occur within the first minute after admitting the gas, will not lead to an appreciable error in the determination of the heat of adsorption.

Fig. 2.



The heats of adsorption of hydrogen on the zinc–chromium catalyst now gave 13·0 cals./g. by the non-adiabatic method and 13·3 cals./g. by the adiabatic method, indicating that the gradients across the adsorbent were very much smaller. It was not possible to make an extensive test of the calorimeter, since the reproducibility of the individual heats could not be made better than ± 0·5 cal. This lack of reproducibility was probably due to variations in conditions of baking out.

The calorimeter is reasonably satisfactory if the gas pressure does not fall below 5×10^{-3} cm., and providing the gas be uniformly distributed throughout the adsorbent, which occurs when the adsorption is a slow process. A number of results have been obtained with it, and these are recorded in the following paper. It may, however, prove to be unsatisfactory if the adsorption is a rapid process leading to a high vacuum within a few minutes, especially if this is coupled with the absence of surface flow within the grains.

Gradients due to Unequal Adsorption.—The adsorption of oxygen on a reduced zinc–chromium catalyst was found to be a rapid irreversible process, the speed of which is very high, and there is probably little mobility of the adsorbed gas within the grains of the adsorbent. The differential heats of adsorption are found to increase to a maximum, as has been found in other cases by many of the early workers with the thermocouple calorimeter. On admission of the first small amounts of gas to the freshly activated catalyst, adsorption occurs mainly at the top of the container, and the distribution of heat in these circumstances within the calorimeter with a hard vacuum inside it is not sufficiently rapid for the thermocouple to record the average temperature before serious heat losses occur. In consequence, calculation gives a low initial heat. The employment of helium as a carrier gas made matters much worse.

It was found possible to measure the heat of adsorption of oxygen on zinc–chromium by admitting sufficient gas to saturate the catalyst, thereby ensuring a good distribution of gas. Calorimeter 1*e*, however, proves to be unsuitable for the measurement of the differential heats. It was, therefore, necessary to pay more attention to the distribution of gas into the absorbent. Calorimeter 1*f* (Fig. 3) was designed for this purpose.

FIG. 3.

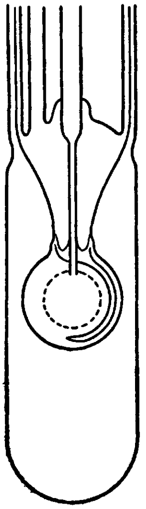
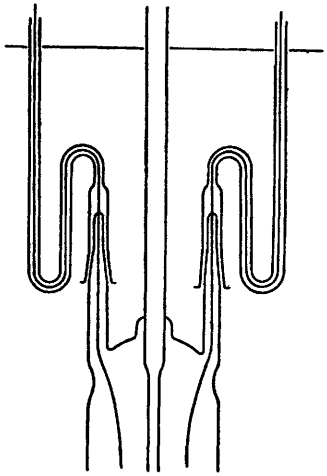


FIG. 4.



Calorimeter 1f.—This consisted of a very thin spherical bulb 3·3 cm. in diameter, containing a platinum-gauze vessel 2 cm. in diameter, the entrance to which was a very thin inlet tube so arranged that the gas could only penetrate to the absorbent through the platinum gauze vessel. This ensured a better distribution of the gas, and, what is perhaps as important, shortened the distances over which it has to travel within the calorimeter. Since the heat capacity of this calorimeter was about half that of 1*e*, the Newton coefficient was about twice as large. As before, the rate of loss of temperature is constant above 5×10^{-3} mm., being 0·046°/min. With a hard vacuum inside the calorimeter, the rate of loss of temperature is 0·038°/min., so the temperature gradients in this extreme case are not very large, and the maximum divergence of the thermocouple temperature from the average cannot be greater than 4 in 46 and is probably much less than this. Provided there be a good distribution of gas, even with a hard vacuum, this calorimeter will give heats of adsorption with a fair accuracy.

The differential heats for the adsorption of oxygen on zinc–chromium oxide were improved in calorimeter 1*f*, but they still showed a maximum, and when successive volumes of 0·16 c.c. of oxygen were added to 3·6 g. of oxide, the maximum occurred at the eighth admission and this probably corresponded to the adsorption of gas in the immediate neighbourhood of the thermocouple.

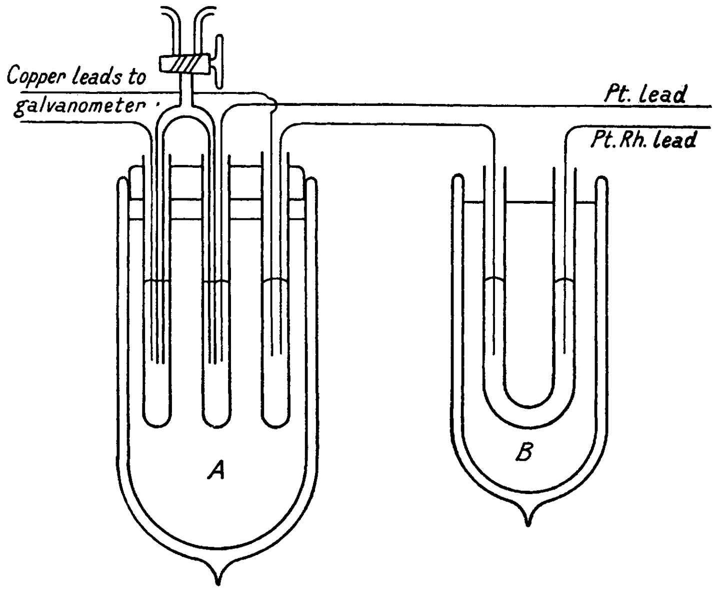
Maximum deflexion	8·5	8·2	8·3	8·3	8·9	9·1	9·7	11·1	10·5	9·3	5·6
Deflexion after 15 mins.	6·8	6·6	6·6	6·3	6·4	6·3	6·6	6·5	6·3	5·7	4·4

The heat is not properly distributed throughout the oxide until after 10—15 mins., and heats calculated at this time will not be very accurate on account of the magnitude of the cooling correction. A mixture of equal volumes of helium and oxygen improved matters somewhat but did not entirely remove the maximum. The adsorption was much slower and hence the maximum deflexion is lowered.

Maximum deflexion	7·3	6·8	6·8	6·9	6·7	6·8	6·9	8·7	8·3	8·2
Deflexion after 15 mins.	6·5	6·1	6·0	5·8	5·7	5·6	5·6	6·0	6·0	4·6

The reason for the failure of helium is thought to lie in its not being adsorbed by the adsorbent. It is unable to enter the grains and improve their conductivity for heat. This was confirmed by measurements of the cooling coefficients with helium in the calorimeter. The loss of temperature with helium as a carrier gas is constant over the pressure range of hard vacuum to 1 mm. pressure, and the conductivity across the grains is not appreciably improved until the pressure of helium is above 1 cm. The reduction of the thickness of zinc oxide to one-third would have given better results, but even then there would be an uncertainty of several per cent. in the results.

FIG. 5.



This is the only case which has given much difficulty. For other rapid processes, such as the adsorption of carbon dioxide on zinc–chromium oxide and ethylene on zinc oxide, the calorimeters worked satisfactorily. In these cases the grain conductivity was probably higher.

EXPERIMENTAL.

Thermocouple and Leads to Galvanometer.—A platinum–platinum-rhodium thermocouple was employed in conjunction with a Kipp and Zonen Z3 galvanometer, and the wires were fused directly through the Pyrex glass (see Figs. 1 and 3). The sensitivity of this galvanometer can be varied; it was usually employed at a sensitivity of 20—25 cm./degree. The deflexion was recorded on a revolving drum placed 2 m. from the galvanometer.

One of us and Kingman (*Trans. Faraday Soc.*, 1931, **27**, 322) observed that on admitting an inert gas to the adsorbent in a vacuum calorimeter, an *E.M.F.* is produced even when no gas is adsorbed. This effect, called the " gas effect," was not understood at the time but was eliminated by surrounding the calorimeter and leads in an air thermostat. Subsequently, D. E. Wheeler (unpublished) and Beebe (*Trans. Faraday Soc.*, 1932, **28**, 761) traced the effect to changes in the temperature gradients along the thermocouple wires, which occur on admission of the inert gas. An *E.M.F.* is produced at a point of strain when there is a temperature gradient along the wire. The point of strain appears to be situated where the wires emerge from the glass, and the trouble can be avoided by surrounding the leads emerging from the seal to a length of 10 cm. in the calorimetric fluid. The arrangement adopted is shown in Fig. 4.

Currents are also produced in the thermocouple circuit by draughts along the leads and on switching in the thermocouple circuit. It is necessary to encase the leads in glass tubes and surround them with cotton wool. A mercury switch (Fig. 5) is employed to eliminate *E.M.F.*'s due to switching in the circuit. Electrical contact is made between the copper leads to the galvanometer and the platinum leads of the thermocouple by raising mercury in the switch A. The switch was immersed in a Dewar vessel containing water which could be stirred by a slow stream of air. The cold junction is shown at B. These arrangements gave satisfactory results except on very windy days.

Calibration of the Thermocouple.—It was found most convenient to calibrate the thermocouple by a variation in the temperature of the cold junction. At 0°, the thermocouple was calibrated by adding a solution of sodium chloride to ice and stirring the mixture until the temperature was constant as shown by a Beckmann thermometer. At 20°, a dilute solution of sodium hydroxide was used as the calorimetric fluid, and a rise in temperature achieved by adding a dilute solution of hydrochloric acid. The individual calibrations agreed within 1%, whether done at the cold junction or at the thermocouple in the calorimeter.

Calorimeters.—These are shown in Figs. 1 and 3. In all cases, except Type I, the inner bulb was made of very thin Pyrex glass which contained the adsorbent and thermocouple. This was fused into an outer cylindrical bulb with walls 0·3 cm. thick. The details of the construction will be seen from the figures. In calorimeters 1*e* and 1*f*, there was a platinum gauze tube or bulb for distributing the gas. The thermocouple wires were usually fused through the walls of the thin bulb, and again through the walls of the outer cylindrical bulb. After emerging into the air, they were immersed in tubes for a length of 10 cm. under the calorimetric fluid. The outer surface of the thin bulb and the inner surface of the outer cylindrical vessel were platinised in the final forms of the calorimeter. The walls of the calorimeter bulb were so thin that it was essential that the difference in pressure between the inside and the outside of the calorimeter should not exceed 1 cm. of mercury. There was no appreciable leak of gas across the walls of the calorimeter within the duration of an experiment, but it was found that some hydrogen gas diffused through the walls of the calorimeter, if a pressure difference of 1 cm. was maintained for 24 hours.

Type I (*Fig.* 1a).—The platinum container weighed 25 g. and was 9 cm. long by 2·2 cm. in diameter. It contained an axial tube of platinum gauze 100-mesh to the inch. It was suspended in the outer cylindrical vessel by 34-gauge copper–constantan thermocouple wires. The weight of adsorbent was 12·3 g. of zinc oxide–chromium oxide and its heat capacity was 2·167 cals./degree.

Type II.—The thin Pyrex bulb in 1*b* weighed 1·7 g. and was 4·5 cm. long. It contained 9·9 g. of zinc–chromium oxide, and the temperature changes were measured with a 46-gauge platinum–platinum-rhodium thermocouple. The inlet tube was of very thin glass 0·7 cm. in diameter. 1*d* has a slightly larger bulb than 1*b*, but has a much smaller inlet tube 0·2 cm. in diameter. 1*e* is similar to 1*d* except that it has a platinum gauze tube along its axis 0·5 cm. in diameter, to facilitate the distribution of the gas. The total weight of Pyrex glass in the bulb was 2·38 g., platinum gauze 0·734 g., and the catalyst 14·8 g. The heat capacity of the system was 2·244 cals./degree. The surfaces were platinised, and the rate of loss of heat from the surface of the bulb when surrounded by a high vacuum was constant at 0·020°/min. for 1° difference in temperature at pressures of hydrogen above 3×10^{-3} cm. This heat loss did not change with time. This calorimeter was used for the measurement of a number of heats of adsorption.

Calorimeter 1*f* consisted of a very thin Pyrex spherical bulb of about 3·5 cm. diameter, in the middle of which was a platinum gauze bulb 2 cm. in diameter with an entrance from above by means of a thin Pyrex tube. Several such calorimeters were made, and the heat capacities of that employed with zinc oxide are as follows: glass, 0·252; platinum 0·038; zinc oxide, 0·736; total, 1·026 cals. The rate of loss of heat from the inner bulb with a hard vacuum outside was 0·038—0·046° per degree for pressures of carbon monoxide above 5×10^{-3} cm. In other cases the rate of loss of heat was 0·016—0·018°.

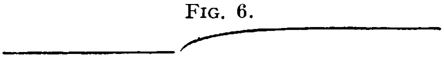
The rate of loss of heat from the inner bulbs of the final forms of the calorimeter was the same whether hydrogen or carbon monoxide was present above the adsorbent, as was also the pressure above which the heat loss becomes constant. The higher accommodation coefficient of carbon monoxide thus balances the higher mobility of hydrogen in the effects of these gases on the conductivity for heat across the inner bulb of the calorimeter.

Experimental Procedure.—The oxide was baked out for 2 hrs. at 460° under high vacuum after every series of experiments. After cooling, it was placed in a thermostat, which consisted of a well-lagged Dewar cylindrical vessel 10 cm. in diameter and 40 cm. high, which was filled with water to such a height that the thermocouple leads were immersed to a length of 10 cm. It was found possible to obtain a sufficiently constant temperature without stirring.

Tests were made of the freedom of the system from gas effects from time to time by admitting inert gases, argon or helium, and none was found. After admitting a gas to the adsorbent, the pressure was read at intervals of 2, 5, 8, 12, and 17 mins., and the rise in temperature recorded photographically. The photographic trace was plotted on a larger scale on squared paper, and the corrections were made for cooling, it being assumed that the time lag on the thermocouple was negligible. Usually the heat of adsorption calculated from the points on the experimental curve were constant after 3 mins. In cases where this was not so, there are reasons for believing that changes are occurring in the distribution of the gas over the surface. These will be discussed in the following paper.

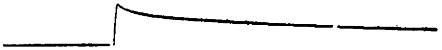
Differential heats of adsorption were measured in some cases by adding successive quantities of gas without evacuation or activation between the experiments, and at the end of a series the heat absorbed on removing the gas was also measured. Typical traces are given in Fig. 6, which includes one showing the peak on the temperature–time curve obtained with carbon monoxide on zinc oxide. The scale of the vertical axis is 6·7 cm./degree, and that of the time axis 0·27 cm./min.

FIG. 6.



Hydrogen on reduced ZnO-Cr_2O_3.

Carbon monoxide on ZnO*: 1st. Admission.*



Carbon monoxide on ZnO*: 2nd. Admission.*

Carbon monoxide on ZnO*: Desorption.*

SUMMARY.

A thermocouple calorimeter is described which is employed to measure the heats of adsorption of gases on oxides. It gives accurate results for total heats of adsorption of both slow and rapid adsorption processes, and is successful for the measurement of differential heats of slow processes. Difficulties are met with in the measurement of the differential heats of rapid processes on account of (*a*) poor distribution of gas throughout the oxide and (*b*) a low grain conductivity. Where the adsorbed molecules are mobile within the capillaries, the grain conductivity is usually sufficiently high to give no serious difficulty. For extreme cases it is necessary to work with a small thickness of oxide.

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