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DIFFERENTIAL HEAT OF SORPTION OF VAPOR ON ACTIVE CHARCOAL.

I. Apparatus and Method of Measurement.

By SETURO TAMARU and KAZUO SATO.

Method of Measurement.

The differential heats of sorption, as well as the isothermal equilibria, of the vapors of ethyl alcohol and benzene on active charcoals of three sorts of different activation, were measured accurately at a temperature of 25°C.

It is a well-known fact that in the case of sorption of vapor on porous material, particularly near the saturated vapor pressure, unusual phenomena even including remarkable hysteresis deviated from a manner of simple plane adsorption are observed. But owing to difficulties of measurement any satisfactory experimental study on the heat of sorption, especially on the heat of de-sorption, to explain these phenomena, seems to have not yet been realized.

After a comparison of various types of calorimeters we have chosen an adiabatic calorimeter as the only satisfactory one for our purposes, because of the benefit that it will catch thoroughly small heat to be developed during a long time, the measurement of the absorbed heat is possible, and charcoal can be heated at a high temperature of 900°C just before the measurement.

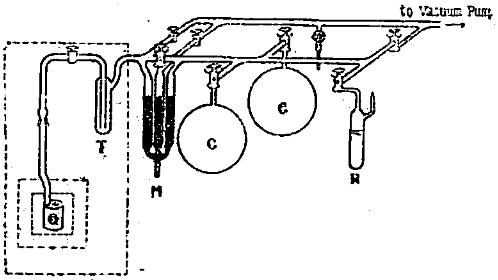

Fig. 1. Apparatus for Sorption System.

In Fig. 1 the system of sorption is indicated. Active charcoal is contained in a silica vessel (Q) and there undergoes the process of purification under the condition of high temperature and high vacuum. Organic liquid, sorptive, is restored at first in a reservoir (R) after several times of vacuum distillation, vaporized into a manometer system (C, M) of known volume to calculate the amount of the vapor from pressure and volume of the system at a definite temperature of an air thermostat, and then sent to the calorimeter system (Q) to contact with the charcoal, being left here until equilibrium is attained. The amount of sorptive on charcoal is calculated as showing the difference of the amounts of the substance in vapor state before and after its contact with the charcoal. From the equilibrium pressure and the sorbed amount at that time, a sorption isotherm is obtained.

At first, vapore pressure is raised stepwise from zero to saturated pressure (ad-sorption process), and then lowered stepwise again to zero pressure (de-sorption process). A trap (T) is used to draw the remaining amount of sorptive from charcoal at low pressure near the end of desorption process by cooling with dry-ice.

The heat amount evolved or absorbed in the charcoal vessel at every step of sorption processes, divided with the sorption increment, is regarded as differential heat of sorption at that state. In this way, at every step of sorption processes the points of equilibrium pressure and the differential heat of sorption are obtained at the same time corresponding to a certain amount of sorption.

The charcoal vessel, Q, is surrounded threefold by the inner and outer boxes and an air chamber, and the heat of sorption evolved or absorbed here is measured as the temperature change of the inner box as compared with the temperature change produced by introducing a known amount of electrical energy. To prevent the interchange of heat with surroundings during the measurement, the temperatures of the outer box and the air chamber are adjusted to hold always within certain small temperature differences from that of the inner box, inspite of the temperature change in this box throughout the measurement. For this purpose, watching the temperature difference between the inner and outer boxes with a thermocouple, the temperature of the outer box is controled by hand introducing suitable amount of electrical heat or cold water. The temperature of the air chamber is made automatically equal to that of the outer box by means of a special temperature regulator.

Structure of the Adiabatic Calorimeter.

The adiabatic calorimeter used consists of, as indicated in Fig. 2, three main parts—a charcoal vessel (Q), an inner box (A) and an outer box (C).

The charcoal vessel is made of silica since charcoal should be previously purified by desorption at a high temperature (900°C) and a low pressure (10^{-2} mmHg), and takes the form of a double-walled cylinder with thin charcoal layer and large surface area, whose wall being as thin as possible (0.5mm) in order to facilitate heat exchange with the outside of the vessel. It contains about 33 cc or 13 g of charcoal.

The inner box is the heart of the calorimeter, being a silver cylindrical vessel of 7 cm in diameter and 10 cm in height and 300 cc of spindle oil whose vapor pressure and specific heat (0.45) is very small. In this box, besides the charcoal

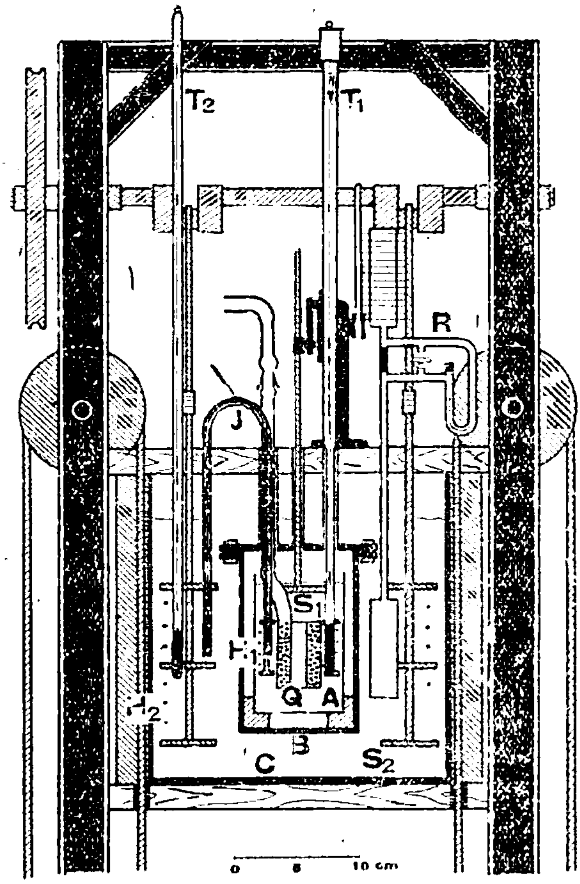

Fig. 2. Adiabatic Calorimeter.

vessel (Q), a Beckmann thermometer (T_1), a vertical stirrer (S_1), an electric heater (H_1) and one junction of a thermocouple are immersed from top into the calorimeter oil. The silver vessel itself is held with thin ebonite plates in a brass-made water tight vessel (B) suspended at the center of the outer box.

The outer box (C) is a large water tank of 10 l content surrounding the brass vessel completely, being covered with thick wooden plates top and bottom, and with felt around. Here a thermometer (T_2), a stirrer (S_2), an electric heater (H_2) and the other junction of thermocouple are inserted from top. For the purpose of cooling the outer box there is an inlet of cold water, not indicated in the figure, which is controlled from the outside of the apparatus. The water tank is hung along a firm pillar against counter balances through pulleys, and therefore is movable vertically very easily. When the charcoal vessel is needed to heat at high temperatures, the surroundings are all very easily removed: the inner and outer boxes and the stirrers downwards, thermometers upwards, and quickly reconstructed.

The above-mentioned apparatuses are as a whole set in an air chamber, whose temperature is made automatically equal to that of the outer box by means of a differential pressure-type thermoregulator (R). The stirrers in the inner and outer boxes are of the up-and-down moving type, consisting of three-storied circular ring plates perforated at several places, and bare nichrome wires are distributed along these plates as electric heaters. This combination of stirrer and heater is very effective to pervade quickly and homogeneously electric heat throughout the box. The stirrers move 124 strokes per minutes in the inner box, and 85 in the outer. Measurement of the temperature change in the inner box is made with a Beckmann thermometer, T_1, of 0.01° scale and read as far as 0.001° with a telescope. Small difference of the temperature between the inner and outer boxes is observed by a differential thermocouple (J), consisting of 6 pairs of Cu-Constantan in series, and a galvanometer, temperature difference of 0.001° corresponding to length of 0.7 mm on a lamp-and-scale.

Adiabaticity of the Calorimeter.

Adiabaticity is the life of an adiabatic calorimeter. Therefore, we examined the effect of the temperature difference between the outer box or the air chamber and the inner box on the temperature of the inner box. The temperature change of the inner box, T_1, under the operation of the stirrer only without sorption process, may be ascribed to three factors: i) friction heat by stirring, q_s [cal/min], ii) heat conducted from the outer box, $K_W(T_W-T)$ [cal/min] and iii) heat conducted from the air chamber, $K_A(T_A-T)$ [cal/min], where T_W and T_A are the temperature of the outer box and the air chamber respectively, and K_W and K_A the coefficients of heat conduction [cal/min°C] between those surroundings and the inner box. Put the heat capacity of the inner box as C [cal/°C], its temperature change in unit time becomes as follows:

$$\frac{dT}{dt} = \frac{q_s}{C} + \frac{K_W}{C}(T_W - T) + \frac{K_A}{C}(T_A - T) \quad [^\circ\mathrm{C/min}]$$

Giving the outer box and the air chamber suitable temperatures respectively we observed the temperature changes in the inner box and obtained the following values as a result of their analysis by the above equation:-

$q_s/C = 0.00077$ [°C/min]
$K_W/C = 0.0124$ [min^{-1}]
$K_A/C = 0.000247$ [min^{-1}]
$K_W/K_A = 50.2$

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The allowable maximum temperature differences between the inner box and the surroundings to hold the temperature error of the inner box below 0.001° during 30 minutes' measurement are accordingly as follows:

Between inner box and outer box: $\triangle T_W=0.0027°$

Between inner box and air chamber: $\triangle T_A=0.135°$

The former corresponds to 2 mm of thermocouple reading and the latter is above the sensibility of the temperature regulator, and therefore it is not difficult to maintain temperature differences below these values. But if a violent reaction should occur in the inner box the temperature difference might exceed the limit temporarily. Suppose the temperature difference attains 30 times of the above limit, and the temperature error of the inner box may still be below 0.001° if the temperature difference can be pushed back within the limit in a minute, and in fact to do this is not a difficult operation.

In conclusion, it was ascertained that with the apparatus used and by the method of measurement adopted the temperature change of the inner box may be observed in the same order of accuracy of Beckmann thermometer. Nevertheless, constancy of stirring may always be demanded, because the temperature change by stirring amounts to 0.02° during 30 minutes.

The Laboratory of Physical Chemistry,
Tokyo Institute of Technology.