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CALORIMETER FOR SIMULTANEOUS MEASUREMENT OF
THERMAL PROPERTIES AND DIMENSIONAL CHANGES

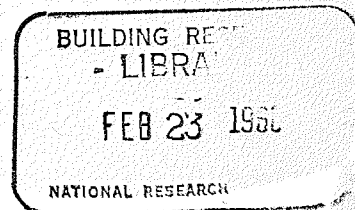
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A. A. ANTONIOU AND G. G. LITVAN

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UN CALORIMETRE POUR MESURE SIMULTANEE
DES PROPRIETES THERMIQUES ET DES
CHANGEMENTS DIMENSIONNELS

SOMMAIRE

Les auteurs décrivent un calorimètre permettant de mesurer simultanément la capacité calorifique et les variations de longueur des systèmes adsorbant-adsorbat entre +25 et -45°C. Ils indiquent quelle est la chaleur spécifique du chlorure de sodium entre 0 et -28°C, et l'on constate que celle-ci concorde à 0.6 pour cent près avec les chiffres obtenus précédemment. Le calorimètre peut également servir à des études sur les chaleurs d'adsorption et les réactions à l'état solide telles que l'hydratation et le passage d'une phase à une autre.



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Calorimeter for Simultaneous Measurement of Thermal Properties and Dimensional Changes

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(Received 1 February 1967; and in final form, 10 July 1967)

A calorimeter is described for the simultaneous measurement of the heat capacity and length changes of absorbent-adsorbate systems between $+25$ and -45°C . The heat capacity of sodium chloride between 0 and -28°C is given and is found to agree with previous results within 0.6% . The calorimeter is also suitable for studies of heats of adsorption and solid state reactions such as hydration and phase transition.

IN the study of surfaces, most investigations are carried out by measuring a single parameter at a time. Correlating the results obtained from isolated investigations of the same system implies that the state of the adsorbent and adsorbate is uniquely defined by the usually measured parameters, temperature, pressure, surface area, and adsorbed amount, but this is not always the case. The history of the system or even the rate at which changes are brought about may have a marked effect on its properties. It is most desirable, therefore, to measure simultaneously as many properties as possible, one of them preferably specific heat, because of its fundamental nature.

In view of this, the detailed description of a calorimeter in which thermal properties and dimensional changes of solids can be measured simultaneously seems to be warranted. It has been used successfully for phase change studies of adsorbates between -40 and $+5^{\circ}\text{C}$,^{1,2} but it is also suitable for studies of heats of adsorption and solid state reactions such as hydration.

EXPERIMENTAL

The calorimeter was of the adiabatic type, which is the best suited for experiments of long duration such as reaction studies. For the measurement of dimensional changes, a Tuckerman optical extensometer (made by Aminco) best met the requirements of high sensitivity, relatively small heat capacity, and easy adjustability.

The extensometer is essentially an optical lever incorporating two mirrors oriented at right angles to each other, one of which is fixed and the other (lozenge) rotatable. A light beam generated in the Tuckerman autocollimator is incident on the fixed mirror, reflected to the rotatable mirror and back to the autocollimator telescope. The position of the image on the reticule scale is a function of the lozenge rotation caused by the dimensional changes of the specimen.

The calorimeter design differed from the conventional in at least two aspects: (a) Windows had to be incorporated

to provide an optical path, and (b) provisions had to be made for easy assembly and disassembly for exchanging the specimen and adjustment of the extensometer between runs. For this latter reason the calorimeter was made of two parts and an O-ring used to form the seal.

These requirements resulted in a calorimeter vessel with an unfavorably large heat capacity compared with that of the system to be investigated and, therefore, high precision was demanded in temperature measurement and temperature control of the environment. In addition, the temperature controls had to be reliable for long periods of time because equilibrium could only be reached in a period of hours. Consequently, it required a period of 2 to 3 weeks to cover a temperature range of 40° . During this time the temperature of the system had to be controlled with precision, at times without supervision.

CALORIMETER ASSEMBLY

The calorimeter vessel C (Fig. 1) which contained the sample A was surrounded by an adiabatic envelope D. The platinum resistance thermometer E was attached to a reference block F outside the envelope and the assembly

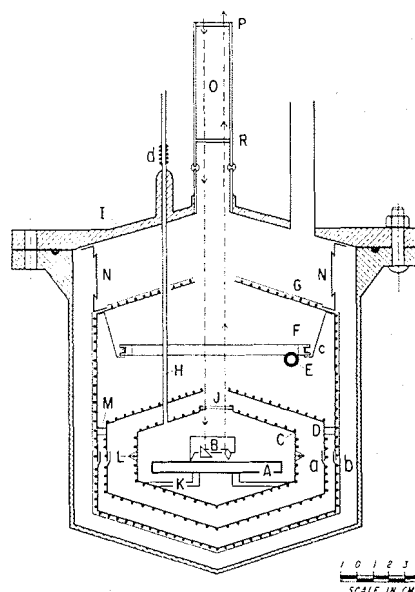


FIG. 1. Schematic diagram of calorimeter assembly.

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¹ A. A. Antoniou, *J. Phys. Chem.* **68**, 2754 (1964).

² G. G. Litvan, *Can. J. Chem.* **44**, 2617 (1966).

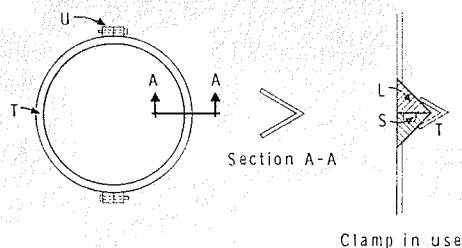


FIG. 2. Schematic diagram of V clamp for calorimeter flanges. L—flanges; S—groove for O ring; T—ring clamp; and U—tightening screw.

was enclosed in a second envelope G, which is called the shield. A similar design was used by Osborne and Ginnings.³

The whole assembly was enclosed in the vessel I and was immersed in an ethyl alcohol bath. The shield, the envelope, and the calorimeter were constructed of two parts so that the lower ones could be removed without greatly disturbing the electrical wiring.

The size of the calorimeter⁴ C was determined by the size of the sample A ($70 \times 10 \times 5$ mm), and the extensometer B ($30 \times 15 \times 15$ mm). It was spun of brass, had a wall thickness of 0.025 cm, and a volume of 290 ml. The vacuum seal between the upper and lower parts was attained by the flanges L and a silicon rubber O-ring (Armet Industries 205A), which proved to be satisfactory in the working temperature range. In order to keep the mass of the calorimeter as small as possible a special ring clamp of two halves with a V cross section was used instead of bolts (Fig. 2). By tightening the screws U, the circumference of the ring was reduced, pressing the flanges together.

The upper part of the calorimeter contained a 3.75 cm diam quartz window J (Fig. 1). The edge of the glass was platinized and then sealed to the vessel with Silastic cement. The calorimeter could be evacuated and vapors admitted through a stainless steel tube H.

A Tuckerman optical extensometer and sample were mounted on a copper holder K; a set of vanes improved the heat transfer.

The envelope D (Fig. 1), and the shield G, were made of brass, 0.040 cm thickness, in two parts. They were held together by a sliding joint, a and b. The envelope and the shield were thermally shunted by a ring M.

The reference block F was machined of brass and the heater wire was wound in a recessed cavity C. Copper shims were placed between the windings to improve heat conduction. The platinum resistance thermometer E was housed in a copper sleeve, which was soldered to the block. Both the reference block and the shield were suspended from the lid of the outer vessel I by Bakelite spacers N.

Evacuation of the space O between the two quartz windows P and R prevented frost formation.

The vessel I containing the assembly was placed in a Dewar flask filled with ethyl alcohol. The bath was cooled by a two-stage compressor and stirred by injecting dry air (Gilbarco heatless air dryer). The bath was kept at a temperature lower than that of the calorimeter in order to provide a heat sink for the shield and the envelope.

ELECTRICAL WIRING

The B & S 36-gauge constantan heater wire was bifilarly wound and attached with Glyptal resin to the outer surface of the upper and lower parts of the calorimeter. It was covered with aluminum foil to reduce radiation losses and then baked at 150°C . The resistance value of the heater was $280\ \Omega$. The heater of the envelope and shield were made in a similar fashion.

The copper and constantan wires of the thermopiles were B & S 36-gauge insulated with silk. Their length was approximately 13 cm between the calorimeter and envelope and 12.7 cm between the calorimeter and reference block. The ends of the wires were twisted and soldered with thermal-free solder to 0.0025 cm thick small copper shims, which were attached to the aluminum foil with a thin coat of Dow Corning Silastic 731. This method proved to be not only convenient, but also satisfactory, because of the Silastic's excellent bonding strength over the range of temperature changes, and because of its very good electrical insulating properties. As the lower part of the calorimeter had to be removed between runs, the thermocouple junctions were detached by applying the clean tip of a soldering iron, which caused practically no change in the amount of solder on the shims. The surface of the calorimeter was divided into seven thermal zones and the shims of the thermocouples were placed in each one, thus averaging the temperature of the total surface. The lead wires of the calorimeter heater were thermally attached to the stainless steel tube H for a length of 15 cm. The temperature along the tube was controlled with heater at d so that heat exchange with the calorimeter along these leads was prevented. All the other leads were thermally

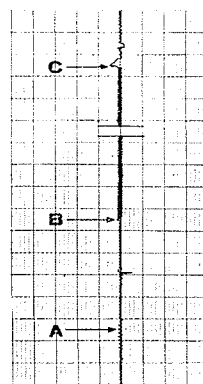
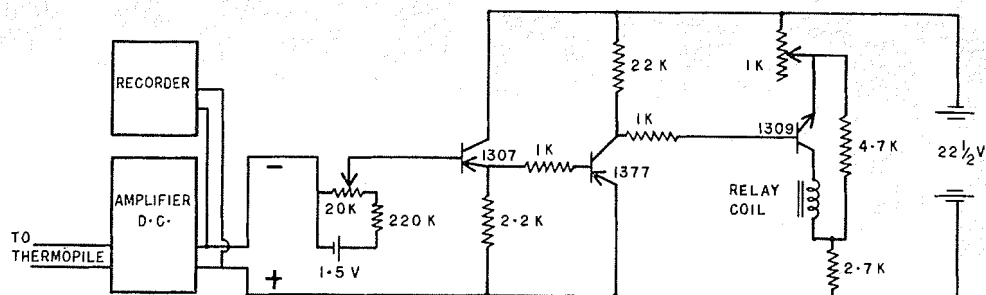


FIG. 3. Section of calorimeter-envelope control chart. A—fore-period, B—start of run, C—end of run and start of afterperiod. The smallest division represents 0.002°C temperature difference.

³ N. S. Osborne and D. C. Ginnings, *J. Res. Natl. Bur. Std.* **39**, 453, RP 1841 (1947).

⁴ The term calorimeter is reserved for only the vessel, C, and the whole assembly, from A to G, is referred to as the calorimeter assembly.

FIG. 4. Schematic diagram of transistor relay circuit.



anchored to the upper part of the shield, then to the lid of the outside vessel and fed through a vacuum seal formed in a glass tube with Picein wax.

TEMPERATURE MEASUREMENT AND CONTROL

The temperature of the calorimeter was determined by measuring the temperature of the reference block and the difference between that and the calorimeter. A Leeds and Northrup platinum resistance thermometer (calibrated by the Division of Applied Physics, National Research Council, Canada) was used in conjunction with a L and N model G-2 Mueller bridge. A seven-junction copper-constantan thermopile measured the temperature difference; the emf was amplified with a Keithley model 149 microvoltmeter. The amplified output activated a sensitive relay⁵ operating at 1.5 mA and heated the reference block with high or low current. The apparent temperature difference between the block and the calorimeter was less than 0.0001 C°.

Adiabatic conditions were achieved by an on-off type of control system governed by a seven-junction copper-constantan thermopile between the calorimeter and the envelope. The emf of the thermopile was amplified and fed into a Speedomax 0.1 mV recorder. The slidewire shaft of the recorder equipped with a control disk actuated a microswitch in the heating circuit. By proper adjustment of the low and high heating current, the temperature difference between the envelope and the calorimeter was ± 0.001 C°. Figure 3 shows the type of control achieved during a run.

Isothermal conditions along the tube were maintained by a high-low type control. Again, a seven-junction copper-constantan thermopile between the calorimeter and points of the tube some 8 cm away from it served as a sensing element. The emf was amplified by a Leeds and Northrup model 9835B microvolt amplifier and fed into a transistor relay circuit⁶ shown in Fig. 4. By supplying an additional bias from a dry cell, it was arranged that $\pm 0.3 \mu\text{V}$ was sufficient to operate the relay. The heater controlling the temperature along the tube was placed

outside the vessel, I at d. This prevented not only heat flow to and from the calorimeter, but the formation of a cold spot that could have resulted in the distillation of the adsorbate from the specimen.

The temperature of the bath was controlled by a five-junction copper-constantan thermopile between the bath and the calorimeter and the emf was amplified again by a Leeds and Northrup microvolt amplifier, and its output fed into a relay circuit similar to that used for controlling the temperature of the tube. By appropriate selection of the applied bias voltage, the temperature difference between the bath and the calorimeter could be maintained at a selected value.

The energy input was determined conventionally by measuring the voltage drop across a 1 Ω standard resistor in series with the heater circuit and across a voltage divider with a Leeds and Northrup K-3 potentiometer. The time was measured with a precision synchronous clock and could be read to 0.01 sec.

OPERATION

The calorimeter could be operated by a single operator. Details of loading are given elsewhere.^{1,2} To determine its rate of cooling, the temperature drift of the calorimeter was observed for about 60 min. After the energy input, equilibrium was assumed to have been reached only when the same temperature drift was observed as before. The heater of the calorimeter and the clock were energized through a multiple contact relay (6 HX, Sigma Co., Braintree, Mass.).

PRECISION AND ACCURACY. HEAT CAPACITY OF SODIUM CHLORIDE

The precision and accuracy of the calorimeter were determined by measuring the heat capacity of a sodium chloride single crystal (obtained from the Harshaw Chemical Co.).

The heat capacity was determined at 16 different temperatures and the regression line obtained. The molar heat capacity C_p (cal deg⁻¹ mole⁻¹) in the range between 242 and 273°K is given by the following expression

$$C_p = 9.8927 + 7.127 \times 10^{-3} T,$$

⁵ Relay model SV-1C-2200D, made by the Advance Electronic and Relay Co., meets this requirement.

⁶ Part of the circuit was developed by J. H. McGuire, NRC, which is gratefully acknowledged.

where T is the absolute temperature in Kelvin degrees. The standard deviation was $0.045 \text{ cal mole}^{-1}$. The smoothed values at selected temperatures shown in Table I are 0.3% higher than those of Clusius *et al.*⁷ and 0.6% lower than those of Morrison and Patterson.^{8,9}

COEFFICIENT OF LINEAR THERMAL EXPANSION OF SODIUM CHLORIDE

The average coefficient of linear thermal expansion of the sodium chloride single crystal was found to be $3.80 \times 10^{-5} \text{ K}^{-1}$ in the temperature range of 260 and 280°K . This value deviates by 2% from the average value found by Meincke and Graham.¹⁰

⁷ K. Clusius, J. Goldman, and A. Perlick, *Z. Naturforsch.* **4a**, 424 (1949).

⁸ J. A. Morrison and D. Patterson, *Trans. Faraday Soc.* **52**, 764 (1956).

⁹ T. H. K. Barron, A. J. Leadbetter, and J. A. Morrison, *Proc. Roy. Soc. (London)* **A279**, 62 (1964).

¹⁰ P. P. M. Meincke and G. M. Graham, *Can. J. Phys.* **43**, 1853 (1965).

TABLE I. Molar heat capacity, C_p , of sodium chloride.

T	C_p
242.0°K	$11.623 \text{ cal deg}^{-1} \text{ mole}^{-1}$
246.0	11.650
249.0	11.670
253.4	11.704
255.0	11.712
260.6	11.751
262.5	11.765
267.5	11.798
273.0	11.837

The extensometer's sensitivity, $\Delta L/L$, is 4×10^{-6} as calibrated by the manufacturer.

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