A High-Pressure Calorimeter for Specific Heats of Aqueous Solutions Up to the Critical Temperature[1]

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Studies of the heat capacities of aqueous solutions of electrolytes near room temperature, made to test theories of the nature of these solutions, have been summarized recently by one of us (2). Since the complications of hydrogen bonding in water decrease at high temperatures, we determined to study the heat capacities of solutions of typical electrolytes up to the critical point of water, 219 atm., 374.18°C., using the adiabatic twin-calorimeter method previously developed by the senior author and his collaborators (3). Two nearly identical calorimeters, containing respectively known quantities of solution and of water, are surrounded by an adiabatic jacket to minimize heat losses, and heated electrically. The heaters are connected in series and their resistances can be varied in steps so that the resistance ratio, and hence the ratio of the energy inputs, can be adjusted to equal the ratio of the total heat capacities of the two calorimeters. The heaters form two arms of a Wheatstone bridge by which the resistance ratio can be measured accurately. After correcting for the small thermal unbalance, the resistances of the heater leads, and the heat capacity of the calorimeters, the specific heat of the solution can be determined relative to that of water at the same temperature.

Since the heat capacity of water has been determined up to the critical temperature by Osborne, Stimson, and Ginnings (4, 5), it serves as a convenient reference substance in our system. In order to work with single-phase liquids in the calorimeters, we determined to make the measurements at a constant pressure, greater than the equilibrium vapor pressure of water at each temperature. Our measurements require bomb calorimeters capable of withstanding high pressures, an arrangement for bleeding off excess liquid as the temperature rises, and many other complications not experienced at temperatures below 100°C. This progress report describes the design and some preliminary tests of the new calorimetric equipment.

Bomb Calorimeters

The bomb calorimeters shown in Fig. 1 are cylinders 6 cm. long and 6 cm. inside diameter, with hemispherical ends, and hold 275 cc. They are made from Elastuff 44, a high-temperature steel, with a wall thickness of 6.4 mm., giving adequate strength for vessels of this favorable shape. Each is fitted with a platinum-clad nickel liner *L* to prevent corrosion by electrolytic solutions at high temperature. The calorimeters are made in two halves, threaded right- and left-handed respectively, so that they can

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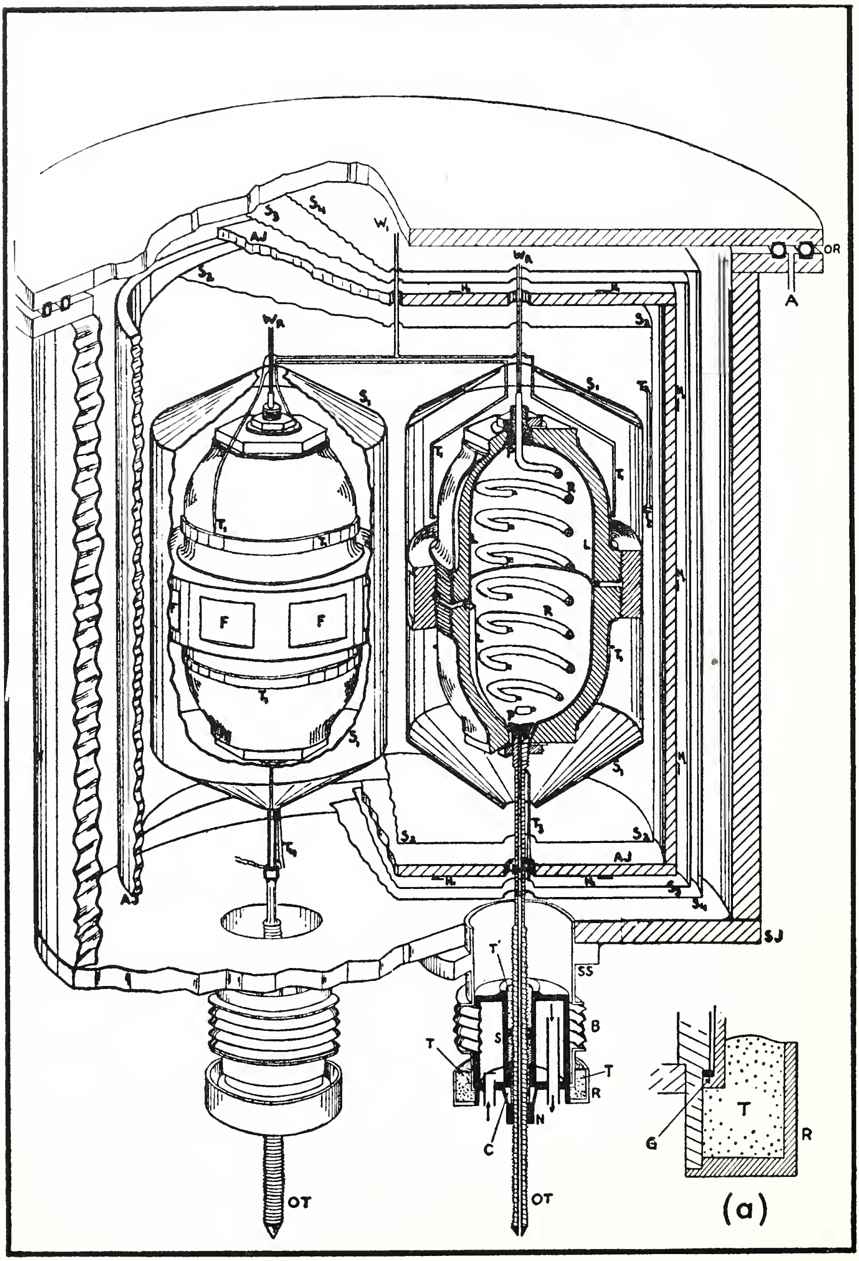

Fig. 1. Calorimeters, radiation shields, and jackets.

be screwed together by a threaded belt. The halves are held by their hexagonal ends in a special vise, while the belt is rotated by an octagonal wrench fitting the surfaces F so that the two halves are pressed together on a platinum gasket 1 mm. thick, without relative rotation which could shear the lip of the liners. The spherical section of each liner ends in a tapered nipple of pure platinum into which fits a tapered platinum plug P. In each calorimeter the upper plug carries a platinum tube incasing the heater while the lower one is fastened to the platinum-lined outlet pressure tube OT. We encountered great difficulty in getting tight seals with these plugs until after very careful grinding with a mixture of fine jeweler's rouge and mineral oil. Liquid in the heated calorimeter touches only the platinum liner or joints "platinum soldered" with a gold-platinum alloy. The outlet tubes pass through water coolers, CW, beyond which the liquid is at room temperature and stainless steel tubing is satisfactory.

The adiabatic jacket AJ is made of 13-mm. copper supported by Mycalex studs (not shown) resting on the bottom of the 10-mm. steel jacket, SJ. The temperature of the adiabatic jacket is controlled by means of evenly-spaced heaters H_1 of nichrome or constantan ribbon or wire insulated with woven glass, mica, Mycalex, or Micamat, all of which unfortunately are fragile and brittle.

A Leeds and Northrup Type 8164-A platinum resistance thermometer (not shown) in contact with the adiabatic jacket, is used to determine the experimental temperature. Differences in temperature between the various parts of the apparatus are measured with chromel-constantan thermels, for maximum sensitivity. A 20-junction thermel T_1, with junctions spaced around the two halves of each calorimeter, measures the difference in temperature between the calorimeters, while four-junction thermels T_2 measure the difference between each calorimeter and the adiabatic jacket, and similar four-junction thermels T_3, T_4 measure the difference in temperature along the outlet tubes.

Since radiation losses become more important than conduction at high temperatures, each calorimeter is surrounded by a 0.01 mm. silver radiation shield, S_1, and the adiabatic jacket is lined with aluminum foil S_2 and surrounded by two aluminum radiation shields, S_3, S_4.

Conduction along the solid connections between each calorimeter and its environment is minimized by suspending it from the lid of the adiabatic jacket by means of an Inconel spring and very fine Inconel wires (not shown), using as fine wire as possible for heater leads and thermels, and especially by reducing each outlet tube to 3 mm. o.d. for a considerable distance, and supplying it with a separate heater H_2 to keep its temperature the same as the base of the calorimeter, as measured by the thermels T_3 or T_4. Gaseous heat conduction is minimized by evacuating the entire steel jacket.

Vacuum

Heat losses by gaseous conduction are known to be proportional to pressure between 1 mm. and 5 microns (1). Below 1 micron, they are negligible compared to radiation, hence we aimed to maintain the vacuum in this range. A D.P.I. Type MCF-60 oil diffusion pump, backed by a mechanical forepump, is connected to the bottom of the steel vacuum jacket through a large tube not shown in Fig. 1. The top of the jacket is sealed with two concentric O-rings, *OR*, the annular space between which is evacuated through a connection *A* to the forepump, to reduce leaks at the seal. The outlet tubes *OT* are fastened with seals which can be broken to remove the calorimeters. Each tube passes through a sleeve *SS*, welded to the jacket and silver-soldered to a flexible Sylphon bellows *B* carrying a brass sleeve at the bottom. A small water cooler slips over tube *OT* to bear against the (crosshatched) threaded sleeve *S*. The connection is made tight by varnishing the threads, filling the narrow trough T_1 with Woods metal, and compressing a Teflon cone *C* against the bottom of the cooler with a brass retaining nut N. As shown in detail (*a*), the cooler is sealed to the bellows by a thin rubber gasket *G* compressed between a recess on the outside of the cooler and the lip on the sleeve at the bottom of the bellows. This joint is submerged in a Woods metal trough *T*, formed by the removable rim *R*. During operation, a controlled flow of water is circulated through the coolers; during assembly or disassembly, this is replaced by steam to melt the Woods metal seals.

The electrical leads, W_1, W_R, etc., about 80 in number, pass through a tube in the top of the jacket (not shown in Fig. 1) connected to a brass junction box, 25.4 x 8.9 x 8.9 cm., with a removable lid sealed by a thin rubber gasket and a Woods-metal trough of the type described above. All of the power leads are fastened to silver studs held in a Mycalex plate. These in turn are connected to the insulated Kovar rods of Stupakoff vacuum seals soft-soldered in the side of the box. The leads of the thermels and platinum resistance thermometer go directly through the Kovar tubes of similar seals so as to avoid soldered junctions which may produce parasitic emf's where the temperature gradient is so large.

The vacuum is measured by means of a large McLeod gage covering the range of 30 to 0.001 micron, connected to the junction box as far as possible from the pump, so that it would give an upper limit to the pressure in the system. After coating all of the Woods metal seals, lead-in seals, and high-vacuum tubing with Glyptal, we obtained satisfactory operation. The diffusion pump could be started less than a half hour after the forepump, and the ultimate vacuum obtained within about two hours. After packing the tops of the five vacuum stopcocks with the Apiezon grease, a vacuum of 0.05 micron was obtained, and the apparatus was operated for several weeks at about 0.2 micron.

Auxiliary Equipment

Fig. 2 is a schematic diagram of the whole apparatus. The outlet tubes from the calorimeters pass through the coolers *CW* and are connected to high-pressure crosses, each equipped with a safety blow-out disc *BO*. A side connection from each tube leads to a combined inlet and bleeder valve through which the calorimeter is filled with water or solution from the appropriate glass flask *SF*, or evacuated through the vacuum pump *VP*. The connections at the bottom of the crosses lead to glass capillary tubes which serve as level gages *LG* where the meniscus between the water (or solution) and a mercury column is visible. The

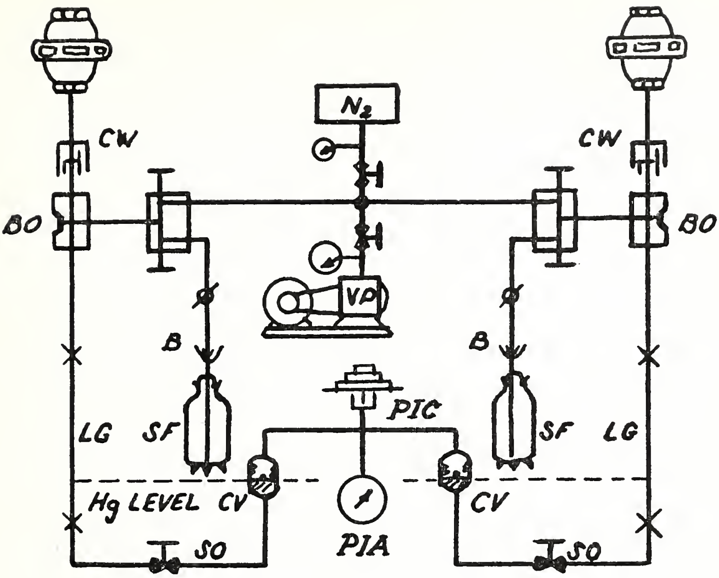

Fig. 2. Auxiliary equipment for calorimeters.

mercury columns extend through U-tubes to an oil pressure line. In each case the mercury-oil meniscus serves to control the operation of a ball check valve *CV* which prevents the loss of liquid from both calorimetric systems in case of the failure of one. The oil pressure lines join in a cross to which is connected a Bourdon pressure indicator and alarm *PIA* and a dead-weight pressure indicator and control *PIC*.

The two flasks *SF* are attached to the bleeder valves through seals made tight with compressed O-rings, while ball-and-socket joints *B,B* in their stems can be loosened to permit weighing for a gravimetric material balance. Pressure in the calorimeters can be generated either by thermal expansion due to heating or by a hydraulic cylinder (not shown) attached to the dead-weight gage.

Safety Devices

In order to operate the apparatus continuously for periods of several days to a week, fully automatic protection must be provided with at least semi-automatic operation while thermal equilibrium is achieved. The safety system shown in Fig. 3 consists of a series of eight servo-mechanical safety devices A_1-A_8 which operate the 6 v. D.C. safety circuit shown in the third row. When everything functions satisfactorily these devices, either directly or through the relays B_1, B_3, B_4, B_5, B_8, actuate the intermediate relay B_9 and through it the power relay B_{10} which completes the circuits to the D.C. calorimeter heaters H_7 and the Powerstats P_1-P_5 supplying the A.C. heaters H_1-H_5. During successful operation, all of the 6 v. lamps L_1-L_8 are off. In case of failure involving any of the eight safety

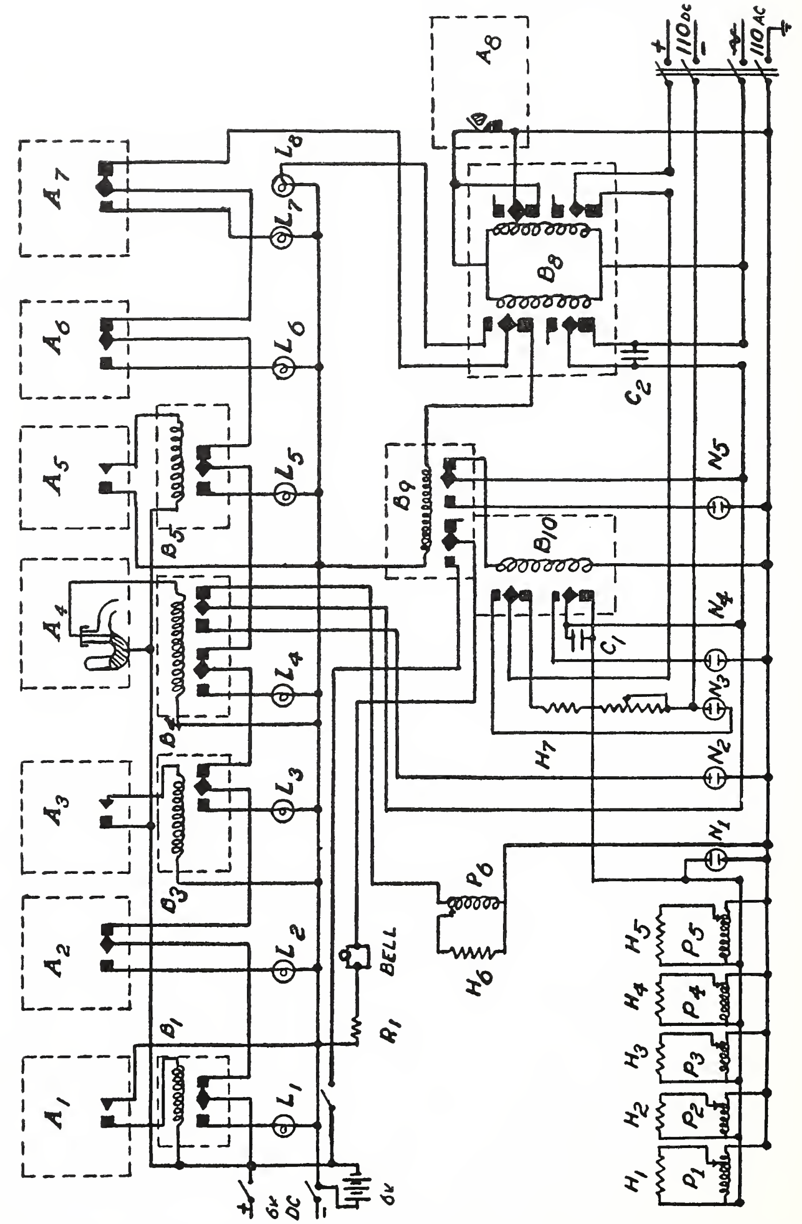

Fig. 3. Safety system. A_1-A_8, safety devices; relays are Potter and Bromfield model KR5D(B_1,B_5), KRP11D(B_4,B_9), and PR11A(B_8,B_{10}) and Clare Series 200(B_3); $C_1 = 0.05$ μfd., $C_2 = 0.01$ μfd. All other symbols are explained in text. All contacts are shown in the position corresponding to satisfactory operation.

devices, the corresponding lamp lights up indicating the defect; relay B_8 is de-energized, causing the alarm bell X to ring and interrupting all power on the heaters of the calorimeters, H_7, the adiabatic jacket, H_1, H_4, H_5 and the outlet tubes H_2, H_3, until the operator corrects the defect. The condition of the power circuits is indicated by a series of neon lamps N_1-N_5, of which only N_1 glows during satisfactory operation.

The different safety devices are: (1) A_1, an adjustable metallic arm attached to a knob in the center of the Bourdon gage which makes contact with the pointer of the gage when the pressure reaches a preset limit, actuating relay B_1. (2) A_2, a microswitch mounted on the deadweight gage with its feeler arm just above the floating piston which rises when the pressure exceeds the weights on the gage, operates the microswitch, and picks up two extra 50-psi weights which prevent further motion. (3) A_3, the metallic contact of a Detect-a-Fire which is set to close at 725°F., actuating relay B_3. (4) A_4, a U-tube containing mercury which rises in the open end to maintain contact with a tungsten wire as long as the pressure in the system remains below about 2 mm. Breaking of this contact deactivates relay B_4 and turns off powerstat P_6. Thus the diffusion pump heater H_6 is interrupted by a vacuum failure. This system is not altogether satisfactory since the jets of the diffusion pump break down at 0.3 mm., and some difficulty was experienced in degassing the mercury in the closed arm of the U-tube, particularly if it is sparked with a Tesla coil. (5) A_5, a mechanical contact closed by the failure of the Mycalex studs supporting the 60-lb. adiabatic jacket. Since Mycalex deteriorates at about 410°C., these studs are backed by slightly shorter broad steel ones which support the jacket if the Mycalex fails. One of these steel studs has a bare wire stretched across its upper surface which closes the electrical circuit and actuates relay B_5 if the adiabatic jacket touches it. (6) A_6, a reset-type microswitch operated by a Lucite piston fitting into a pipe connected to the outside of the blow-out discs. The bursting of either of these at a known pressure of 1500-3500 psi blows the piston against the feeler arm of the microswitch and actuates the safety circuit. (7) A_7, a microswitch controlled by the cooling water, operates the safety circuit if the flow drops too low. The returns of the four coolers for the outlet tubes, junction box, and diffusion pump all pass through a common manifold into a small can with perforated bottom, balanced on a hinged side arm the other end of which is threaded for appropriate adjustable counterweights. A given rate of flow maintains a certain hydrostatic head in the can, which a moderate decrease in the flow of any one of the coolers reduces enough to actuate the microswitch. (8) A_8, a push-button power latch arranged to control the primaries of the two power relays comprising B_8. When the spring-return button is depressed, the relays are activated and the button is by-passed by a connection through the contacts of the right-hand relay. A power failure opens both relays, and they remain deactivated even when power returns to the lines. After a power failure which breaks the vacuum, this arrangement prevents further heating which, in the presence of appreciable air, might disastrously oxidize the surfaces of the adiabatic jacket and shields.

Condensers C_1 and C_2 were put across the contacts of the power relays B_{10} and B_8 respectively, to overcome their tendency to "freeze" under the high self-inductive load of the Powerstats. Normally a battery charger operates the 6 v. D.C. safety circuit; but standby batteries take over in case of a power failure.

Operation

Preliminary measurements showed that the heat capacity of the adiabatic jacket is about 5,000 cal./deg. between 70 and 120°C. Over this interval heat leakage to the surroundings is only about 3 cal./deg.-min., so that 50 watts is sufficient to maintain a constant temperature. The temperature of the steel jacket is barely warm to the touch unless the vacuum is broken when it increases suddenly showing that heat losses by conduction predominate in this range. Mechanical failure of several heater windings showed up quickly during these preliminary experiments but the methods for the filling of the bombs, bleeding out liquid to maintain constant pressure, and keeping track of the solution level proved satisfactory.

Summary

A high-pressure calorimetric apparatus has been built to measure the heat capacities of aqueous solutions up to the critical temperature of water. Variable resistance heaters balance the temperature change of a bomb calorimeter containing solution against that of a similar tare calorimeter containing water. Thermal leakage to the surroundings is reduced by a vacuum jacket and radiation shields, while an automatic safety system guards against experimental hazards. The apparatus is described, and some information is given about its operation.

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