Determination of Heat Capasity of Liquids in Temperature Broad Range
(Principe of calorimeter works)

In the most sensitive high-precision microcalorimeters, to which pertain also commercial instruments DASM-1M, DASM-4, DASM-4A, PDSC, DSC and others the several closed shells are used comprised one into another. The latter are heat shields from the heat-conducting metal (silver, copper), which have on external surfaces the uniformly distributed heaters.

The loading of the both calorimetric chambers by the equal certain amount of the substance under investigation and the standard material, as well as the problem of the free volume are the most complex problems in the differential microcalorimetry. It is easy to see that when one has to do with the measurement of the difference heat capacity with the accuracy of order of 10^{-5} J/K, the accuracy of the loading of the both chambers of the instrument must be not less than 10^{-5} grams. It is practically impossible to obtain this by the weighting of a liquid, flooded in chambers.

Calorimeters with the extractable chambers, as a rule, do not give reproducible results: after the reloading of chambers they change the position and the slope of the registered line of the temperature dependence of the seen difference heat capacity. That is why such sort of instruments, sensitive to the sufficiently abrupt changes of the heat capacity with temperature, in principle can not be used for the determination of the value of the difference heat capacity and its dependence on temperature. In other words, they are not the precision instruments for the determination of the differencce heat capacity of liquids.

The free volume in chambers, staying above the liquid, generates not less difficulties. It is clear that a hermetic chamber cannot be filled completely, since the heat expansion coefficient of chamber and that of the liquid are different. But if free volume is left in a chamber, the additional vapouration occurs in the process of liquid heating-up for what the additional energy disperses.

Though the vapour elasticity above the solvent and diluted macromolecule solution differs insignificantly, the difference heat effect of vaporization turns out to be appreciable because of the enourmous vaporization specific heat (of the order of 2 300 J/g for water). This effect grows with increasing of the free volume; on the other hand, the reduction of the free volume leads to a number of other complications connected with the heat expansion of liquid at heating-up. thus, it is not so easy to take a heat effect of the free volume into account. At the same time, when we

have to do with the superaccurate measurements, the inaccuracy contributed by the effect of the free volume turns out to be not neglectable.

The noted problems were solved by the transition from the measurement of the heat capacity of the certain mass of substance to the measurement of the substance of certain volume. Herewith the volume of liquid is fixed by the hard volume of the calorimetric chamber. The main condition, which must be satisfied, consists in the requirement that the chamber must be filled wholly - even microscopic air bubbles must not be left in it.

For the excluding of bubbles in calorimeter chambers the extra pressure of several atmospheres is applied, and the whole measurement is realized under this extra pressure. As far as the pressure is not large, it does not influence heat characteristics of the solution. At the same time, it completely excludes the arising of gas bubbles at the heating-up of the liquid, since the pressure of the gas, soluted in the liquid is lower than the extra pressure, created by the monostat. Besides, the extra pressure allows to shift essentially the boiling temperature of the liquid under investigation and, thereunder, to shift an upper limit of the scanning temperature range.

In the process of heating-up of à scanning calorimeter with the completely filled chambers the liquid is forced out because of the heat expansion. Hence, the mass of liquid in the working volume of the chamber is decreased with the temperature raising. However, at working with the diluted solutions which have practically the same heat expansion factor, as the solvent has, the forcing out of liquid from the both chambers occurs almost in the same degree and does not influence the result of measurement of the difference heat capacity.

Such principle of measurement of heat capacity of liquid of fixed volume was used in the precision scanning microcalorimeters DASM-1M, DASM-4, DASM-4A, in the ultrasensitive, the so called nanocalorimeters of the type of DSC, PDSC. All these calorimeters have a general principle - undismountability of a measurement chamber. For instance, in the calorimeter DASM-4A, the chambers are made completely from the capillary tube wound in a spiral (Fig). For excluding of the bubbles in such a chamber, to external outputs of the capillary tube the extra pressure of 5 atm is applied which is sufficient for heating-up of the water solution up to150^0C (that is extremely important at the investigation of the thermally stable proteins and nucleic acids rich with G–C- pairs).

Such design of a chamber gives the variety of advantages: first, they can be easier washed and filled with a sample so that no air bubbles are left; second, because of the small diameter of a

tube and its high heat conductivity, the significant temperature swings in liquid filling the tube do not appear in the heating-up process. Consequently, the temperature field in such calorimeter chamber is more uniform and the capillary chambers can be heated-up with the greater velocity, than the bulk ones.

In its turn, the increasing of the scanning rate means the increasing of the real sensitivity of instrument to the changing of the study object. Finally, the capillary chambers bear the vastly greater pressure, than the bulk ones. This allows to raise an upper limit of the working temperature range of the instrument. It reaches 150^0C in the case of water solutions for the instrument DASM-4A.

The ability to scan in both directions along the temperature scale is the important characteristic of the scanning calorimeters. It is inherent almost to all nonadiabatic instruments, having no heat shields. In adiabatic instruments, in which there are heat shields (see Fig.7) the scanning down along the temperature scale requires the controlled tapping of heat.

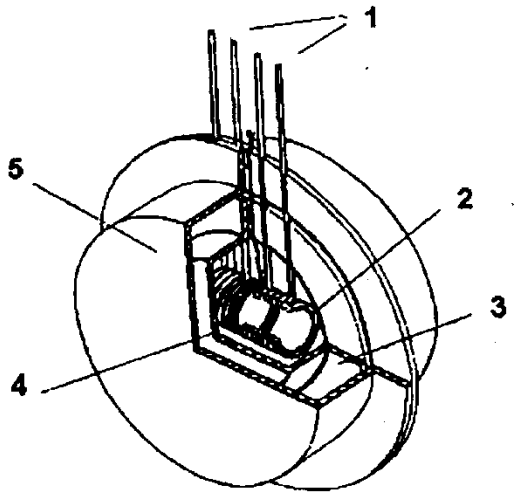

Fig. Calorimetric block of DASM-4A

1-Capillaries of filling. 2-Spiral calorimeteric cell with a heater.

3- Internal adiabatizing shell. 4–Gauge of the temperature

differencebetween the cells. 5 – External heat shield.

This is reached by the shift of heat shield temperature on the certain value with respect to the temperature chamber, which is kept in the whole scanning interval by the watching system.

The lowest limit of the temperature scanning of water solutions is determined by its freezing temperature. The ice formation in solutions deprived of dust and not having crystallization centers begins not under 0^0C, but greatly below: if solution is cooled sufficiently quickly, its possible to overcool it in the liquid condition up to the temperature of order of -10^0C .

The upper limit of the temperature scanning is determined by the boiling temperature, and, hence, by the extra pressure, which the calorimetric chamber can bear without the observable changing of its volume. This limit is significantly higher in the case of capillary chambers which can bear a pressure in several atmospheres in the case of the sufficiently thin wall (and, hence, the small heat capacity).

The calorimetric investigation of the solutions of macromolecules begins with the selecting of the conditions and the preparation of the solution for the study. The conditions are selected coming from stated problems and possibilities of the available instrument. Under they, in the first place, the necessary purity of preparation, the necessary solvent and necessary concentration of macromolecules in solution are implied.

The choice of the optimum of the scanning rate is of the essential importance at the work with the scanning microcalorimeters. At the choice of the heating-up rate it is necessary to take into consideration the following: a) the heat capacity sensitivity of the scanning microcalorimeters is the higher, the higher is the heating-up rate; b) with the increase of the heating-up rate the nonuniformity of the temperature field increases, too.The latter has importance, particularly, at the abrupt process study, which tend to shift to the high temperature side at the too high heating-up rate; c) the rate of the conformation transition of macromolecules is not endless: for the globule proteins it is very high (of the order of 10^3 sec^{-1}), for the fibril ones, for instance, the collagen, it is low enough (of the order of 10^{-2} sec^{-1} and lower). The stability of the shape of the temperature curve of the seen heat capacity at the variations of the rate to the greater and to the smaller side is the main criterion of correctness of the rate choice.

Though the differential calorimeter is created for the measurement of the difference heat capacity of the solution and the solvent, this difference value can not be determined with the high accuracy with the only one measurement because of the incomplete identifity of chambers. For its determinations it is necessary first to fill the both chambers with the one and the same standard liquid (solvent) and define the zero or base instrument line in the whole necessary temperature interval.

The deflections of the base line got at the reloading of the instrument define the accuracy with which the difference heat capacity of the two samples can be determined.

As a rule, on supersensitive instruments the base line is not completely horizontal and straight as far as it is impossible to make the both chambers completely identical. For the rectifying of a base line and reduction it to the zero value, the electronic corrector (or PC) is used, which is a device, rememberring the initial base line of the instrument and subtracting it automatically from the all following measurements before the registration of the measurement result by a grapher (or other way, e.g., PC).

The scanning microcalorimeter DASM-4A, in particular, is provided by the electronic corrector. In the instrument DASM-4 only the general slopping of base, but not its form is corrected.