

DETERMINATION OF THE SPECIFIC HEAT OF EVAPORATION OF A LIQUID
FROM DISPERSED SOLIDS IN A WIDE TEMPERATURE RANGE

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This paper describes a method and a laboratory apparatus for the direct calorimetric determination of the specific heat of evaporation of a liquid absorbed by a dispersed solid in a wide range of temperature and mass content. The heats of evaporation of moisture from KSM silica gel in the temperature range 293°-353° K are determined. The obtained data are used to calculate the relationship between the chemical potential of the absorbed moisture and the moisture content of different temperatures.

The specific heat of evaporation of a liquid absorbed by a dispersed porous solid is one of the main thermodynamic characteristics of the binding of a liquid with a solid [1], and a knowledge of this characteristic is important for both the theory of dispersed solids and drying techniques. Hence, an experimental determination of this quantity is of great scientific and practical interest.

In 1961 one of us [2] proposed a new method and a laboratory apparatus, based on the kinetics of drying, for the direct calorimetric determination of the specific heat of evaporation of a liquid from dispersed solids. This method was successfully used to investigate the specific heats of evaporation of moisture from typical dispersed solids [3]. The apparatus described in [2], however, had several drawbacks, the main one being that measurements of the heat of evaporation could be conducted only in a narrow temperature range. The experience gained in work with the apparatus of [2] led to the construction of a new and much improved apparatus which allowed measurements in a wide temperature range, including room temperatures, which is particularly important for the investigation of thermolabile solids. At the same time, we amended the fundamental principles of the method and made a stricter estimate of the errors which could arise when the conditions of the method were not exactly satisfied. A description of the improvements to the laboratory apparatus, the method of work with it, and the obtained results forms the content of this paper.

The method of determining the specific heat of evaporation of a liquid is based on the continuous automatic compensation of the heat used up on the evaporation of the liquid during the drying of the dispersed solid at a continuously varying evaporation rate.

We consider a sample of dispersed solid subjected to drying in a thermostat in which the air temperature T_a is kept constant throughout the experiment. If there is an electric heater inside the sample, the heat-balance equation for the case of drying will have the form

$$L \frac{dm}{d\tau} + c_p m \frac{dT}{d\tau} + \alpha_q F (T - T_a) - I r = 0. \quad (1)$$

Here the first term takes into account the heat spent on evaporation of the liquid; the second represents the heating of the sample; the third the heat transfer to the surroundings; and the fourth the power released in the sample by the electric heater.

To determine the specific heat of evaporation of the liquid from the sample it is necessary to maintain the current in the sample so that the surface temperature of the sample during the whole experiment is constant (despite the change in evaporation rate in the different drying periods) and equal to the constant ambient temperature. In this case all the heat released by the heater will be spent entirely on evaporation of the liquid, so that from the known current in the heater and the drying rate of the sample the specific heat of evaporation of the liquid can be determined for any mass content of the sample, from the formula

$$L = \frac{I r}{dm/d\tau}. \quad (2)$$

Thus, to determine the specific heat of evaporation of a liquid for different mass contents of the dispersed solid we need to know at any instant during the experiment the drying rate dm/dt , the current I in the sample heater, and the mass content W of the sample, with the main provision that the temperature of the surface of the sample and the ambient temperature be equal.

If the temperature of the sample surface is not exactly equal to the air temperature in the thermostat the heat transfer occurring in this case will introduce into the measured heat of evaporation an error equal to

$$L_{act} - L_{meas} = \frac{\alpha_q F (T - T_a)}{dm/d\tau}. \quad (3)$$

It can be seen from (3) that the magnitude of this error is inversely proportional to the rate of evaporation of the liquid. Hence, although this method can in principle be used to determine the heat of evaporation at any temperature, the determination of the heat of evaporation at relatively low temperatures (e.g., for water at room temperature) on the previously proposed apparatus [2] involved considerable errors, since the evaporation rate in this case is too small, and even a small error in regulation of the temperature of the sample can greatly distort the results. The same limitation applies to the determination of the heat of evaporation of a strongly bound liquid (an adsorbed liquid, for instance), where the evaporation rate is low even at much higher temperatures.

To increase the evaporation rate of liquid in the described new apparatus we can alter the total pressure

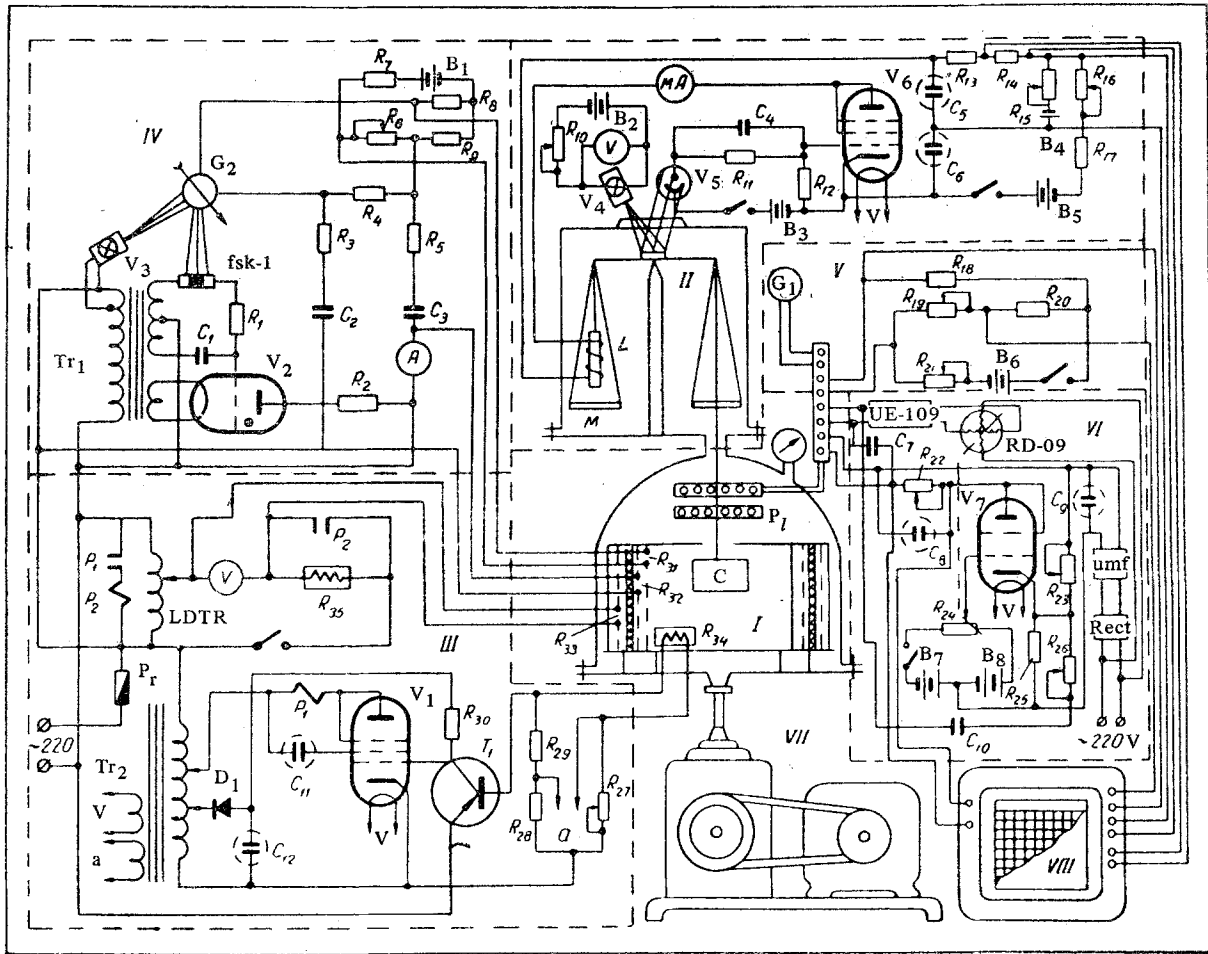


Fig. 1. Diagram of apparatus.

in the thermostat from atmospheric to $(3-8) \cdot 10^3$ N/m². The evaporation rate in this case can be increased several (as much as ten) times, and this allows a considerable extension of the temperature range in which the measurements can be made. It is important that the heat of evaporation of most pure liquids when the total pressure is changed in the above range is practically unchanged [4, 5] and, hence, it is unnecessary to introduce any corrections for pressure in the obtained results.

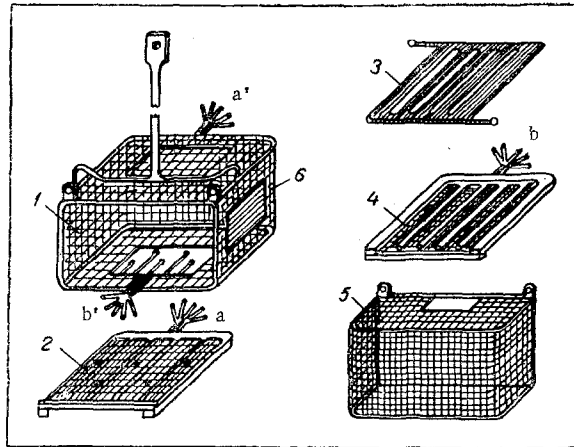


Fig. 2. Calorimetric cell.

It is important that the calculation in this method, as distinct from most other methods used at present, does not involve the heat capacity of the system. This is particularly important for the determination of the heat of evaporation of a liquid from dispersed solids, since the heat capacity of the liquid adsorbed by a solid can differ significantly from the heat capacity of the free liquid [6], and it cannot always be estimated.

A schematic diagram of the new apparatus is shown in Fig. 1. The sample of dispersed solid in the form of powder or sand is put into the calorimetric cell (C in Fig. 1). Its construction is shown in Fig. 2. As distinct from the previously described cell [2], it is in the form of closed copper meshwork box (mesh size 0.2 mm) with soldered supporting edges. Inside the cell, which consists of two parts (2 and 4 in Fig. 2) there is a flat sectioned heater 3 made of nichrome with a resistance of about 1300 ohm. The space between the heater and the meshwork walls of the cell takes about 2-4 g of sample (depending on its density). Since the cell is made of sufficiently fine mesh it can retain a considerable amount of suspended liquid. Thus, at the start of the experiment we can determine the heat of evaporation of the free liquid, which is important for checking the obtained results.

Special experiments showed that the whole surface of the cell, owing to the high thermal conductivity of the copper meshwork, is isothermic, which is essential for the determination of heat of evaporation by the described method. One group of junctions *ab* of a differential ten-junction copper-constantan thermopile is cemented to the outer surface of the meshwork for measurement of the temperature of the cell surface. The second group of junctions of the thermopile *a'b'* is

attached to a closed copper meshwork box (1 and 5, Fig. 2) with a mesh size of 2 mm, which surrounds the cell at a distance of 1.5 cm from it and evens out the air temperature in the thermostat. Thus, the thermopile reacts to a temperature difference between the cell surface and the surrounding air and serves as a sensor for the regulator of the current in the cell heater. A second similar thermopile, consisting of four thermocouples (not shown in Fig. 2), is connected to a separate mirror galvanometer *G*, and is used to check that the temperatures of the cell surface and the air in the thermostat are equal, i. e., it provides a check on the operation of the current regulator.

Instead of the arrangement with the galvanometric amplifier described in [2], the current in the heater of the calorimetric cell is regulated in this apparatus by a proportional astatic regulator represented by block VI in Fig. 1.

The emf of the thermopile mounted on the cell is converted to an alternating voltage by means of a vibrating-reed converter and is then amplified by a UE-109 electronic amplifier. Connected to the amplifier output is an RD-09 reversing motor, the direction and speed of rotation of which are determined by the sign and magnitude of the emf of the thermopile of the calorimetric cell. The spindle of the RD-09 motor is connected through a reducing gear to the slider of a variable resistor, which sets the potential on the grid of a 6P1P tube, the anode circuit of which contains the heater of the calorimetric cell. Any deviation of the temperature of the surface of the calorimetric cell from the temperature of the surrounding air causes the rotation of the reversing motor and a concomitant change in the current in the heater of the calorimetric cell. The rotation of the motor continues until the change in current in the heater makes the temperature of the cell surface equal to that of the surrounding air.

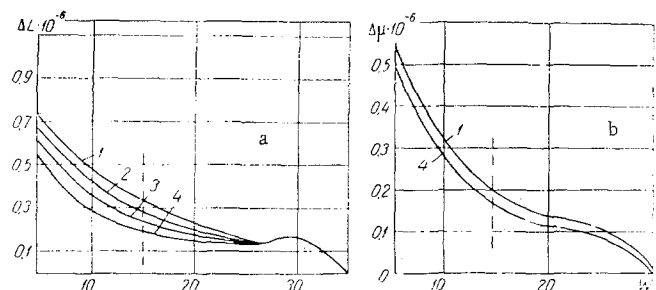


Fig. 3. Increase in specific heat of evaporation ΔL , J/kg (a) and increase in chemical potential of moisture $\Delta\mu$, J/kg (b) at functions of moisture content, *W*, % of KSM silica gel at different temperatures (1-293° K; 2-313°; 3-333°; 4-353°). The vertical broken line denotes the boundary of evaporation of absorbed and capillary moisture.

The inclusion of a reversing motor, which is an integrating link, increases the stability of the regulating system [7] and also makes the regulator astatic, i. e., free from the error of statism. This is the advantage of this regulator over that described in [2], since during

experiments to determine the specific heat of evaporation of liquid bound in different ways with a solid, the current in the heater of the calorimetric cell can vary from 2–3 to 80–100 m, i. e., by a factor of more than 30, and in this case the error of the regulator due to its statism may be considerable [7].

The power amplifier incorporating a 6P1P tube is connected up as a variable-input voltage stabilizer [8]. This considerably reduces the effect of variations of the anode voltage, applied by a dynamotor, on the operation of the circuit. A system of screens, as described by White [9], is used to shield the thermocouples from interference. The current in the cell heater, which comes into the calculation formula (2), is recorded throughout the experiment by an EPP-09 recording potentiometer VIII (Fig. 1).

For continuous recording of the weight of the calorimetric cell with the sample the latter is suspended on one of the pans of an automatic balance (block II in Fig. 1), which is connected up in the same way as in [2]. For convenience in calculating the mass content of the sample and the evaporation rate of the liquid [which come into formula (2)] the balance system has two outputs, the signals from which are applied to different channels of the EPP-09 so that two weight curves are recorded simultaneously on the tape. The first curve, which has a small scale (about 3 g over the whole scale), enables easy calculation of the mass content of the sample at any instant during the experiment. The second curve, recorded on a very large scale (about 100 mg over the whole scale) and consisting of a large number (up to 20) of separate portions "fitted into" the scale by means of a variable resistor R-15 (Fig. 1), serves for accurate calculation of the evaporation rate of the liquid.

The calorimetric cell containing the sample is accommodated in the thermostat (I in Fig. 1), which is in the form of a metal case of 4-mm iron with an airtight door. The mechanical part of the balance is also contained in a sealed iron case connected with the thermostat by a tube through which the suspension of the cell passes.

The air pressure in the thermostat (and the balance case connected to it) is altered by a RUN-200 forepump (VII in Fig. 1). The pressure in the thermostat is regulated manually by a valve and checked by a manometer. The presence of the large fore-cylinder prevents sharp variations of pressure, and the slow change of pressure during the experiment has no effect on the results.

The air temperature in the thermostat is kept constant by means of two independent regulators (blocks III and IV in Fig. 1). Coarse temperature control of the air in the thermostat is effected by a relay regulator (III in Fig. 1) with an R-34 thermistor as the sensitive element [10]. This type of regulator provides better temperature control when the air pressure in the thermostat changes than the contact-thermometer regulator described in [2]. More accurate control of the air temperature near the calorimetric cell, contained in the guard vessel of the thermostat, is effected by a proportional regulator IV similar to that de-

scribed in [2]. The air temperature in the guard vessel of the thermostat is continuously measured by a copper resistance thermometer (6 in Fig. 2) and recorded by means of a bridge circuit V as a check curve on the tape of the recording potentiometer VIII.

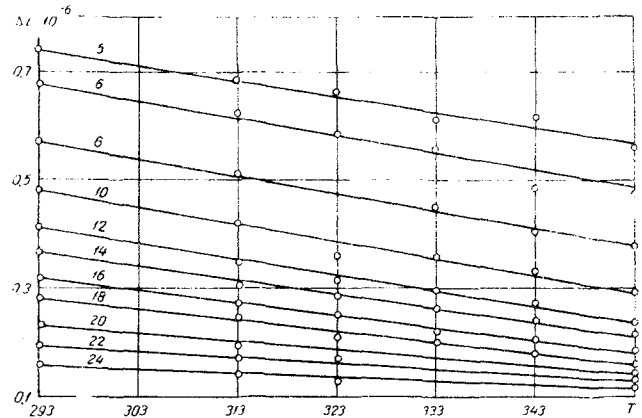


Fig. 4. Increase in specific heat of evaporation of moisture ΔL , J/kg, as a function of temperature T , °K for different moisture contents W , % (figures on curves).

Thus, with this laboratory apparatus we were able to record experimentally the values of all the quantities which are contained in formula (2) and are required for the calculation of the specific heat of evaporation of a liquid from a dispersed solid with any mass content in a wide temperature range. The error in determining the heat of evaporation on this apparatus does not exceed 1–3%, depending on the sample and the experimental conditions.

Using this apparatus we determined the specific heat of evaporation of different forms of bound moisture from a typical capillary-porous solid—KSM silica gel in the temperature range 293°–313° K. The experiments at 333° and 353° K were conducted at atmospheric pressure and those at 293° and 313° K were conducted at an air pressure of about $6.6 \cdot 10^3$ N/m². The obtained results are given in Fig. 3a.

The figure shows that the heat of evaporation increases as the moisture content decreases. This increase attains a considerable value—at 10% moisture content it is about 20% of the heat of evaporation of free water. The course of the curve changes more sharply on transition from one form of moisture binding to another. This is also typical of almost all moist materials.

Figure 3a also shows that the course and shape of the curves are almost independent of the temperature, although the increase in heat of evaporation is different at different temperatures.

Figure 4 shows a relationship which can be represented fairly accurately in a linear form

$$\Delta L = \Delta L^0 (1 - \gamma T + \gamma T_0). \quad (4)$$

The obtained data also enable an easy calculation of the relationship between the chemical potential of the bound moisture and the moisture content at different temperatures. In fact, the chemical potential and the

increase in heat of evaporation are connected by the well-known Gibbs-Helmholtz relationship

$$L - L_0 = \Delta L = \Delta\mu - T \frac{\partial \Delta\mu}{\partial T}. \quad (5)$$

Integrating (5), we obtain

$$\Delta\mu = -T \int \frac{\Delta L(T)}{T^2} dT. \quad (6)$$

If we substitute in (6) the relationship between the increase in heat of evaporation and the temperature in explicit form (3), we obtain

$$\Delta\mu = \Delta L^0 (1 + \gamma T \ln T + \gamma T_0 - cT). \quad (7)$$

The constant of integration c must be found from the known value of the chemical potential at a given temperature. In this work we used the isotherm of adsorption of water vapor on this silica gel at 293° K. Using this isotherm and the usual relationship

$$\Delta\mu = \frac{m}{M} RT \ln \varphi \quad (8)$$

we calculated the relationship between the chemical potential and the moisture content of silica gel at one temperature. Then, from formula (7) we found the constant c which enables us to find the relationship between the chemical potential and the moisture content at different temperatures. The results of this calculation are shown in Fig. 3b. Figure 3b shows that the chemical potential of moisture absorbed by silica gel does not depend greatly on the temperature. This steady increase in chemical potential with reduction in the moisture content of silica gel is also clearly illustrated.

NOTATION

L is the specific heat of evaporation of liquid; L_0 is the specific heat of evaporation of free liquid; m is the mass of solid; τ is the time; c_q is the heat capacity of

solid; T is the absolute temperature; α_q is the external heat transfer coefficient; F is the surface of sample; I is the heater current; r is the heater resistance; $\Delta\mu$ is the increase in chemical potential (over chemical potential (over chemical potential of free liquid at the same temperature); γ is the temperature coefficient of increase in heat of evaporation; T_0 is the fixed temperature (293° K); R is the universal gas constant; M is the molecular weight of liquid; φ is the relative pressure of vapor over material; ΔL is the increase in specific heat of evaporation of liquid (over that of free liquid at the same temperature).

REFERENCES

1. V. M. Kazanskii, IFZh [Journal of Engineering Physics], 9, no. 3, 1965; Ukr. fiz. zhurn., 10, no. 9, 1965.
2. V. M. Kazanskii, IFZh, 4, no. 8, 1961.
3. V. M. Kazanskii, IFZh, 6, no. 11, 1963; 6, no. 1, 1963; DAN SSSR, 146, no. 4, 1962.
4. Collection: Thermophysical Properties of Substances [in Russian], GEI, 1956.
5. Tables of Thermodynamic Properties of Water and Water Vapor [in Russian], VTI, GEI, 1952.
6. A. V. Dumanskii, The Lyophilism of Dispersed Systems [in Russian], Kiev, 1960.
7. V. M. Shlyandin, Elements of Automation and Remote Control [in Russian], Oborongiz, 1954.
8. A. M. Bonch-Bruevich, The Use of Electron Tubes in Experimental Physics [in Russian], GITTL, 1955.
9. W. P. White, Temperature, Its Measure and Control, R. P. C., 1941.
10. Yu. Pukhlik, Radio, no. 11, 1963.

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Light Industry, Kiev