CHEMICAL INSTRUMENTATION

Calorimeter for Measurement of Heats of Solution

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Dedicated to Prof. Dr. Ing. Mikuláš Gregor on the occasion of his 65 birthday

A calorimeter is described for measurement of heats of solution of inorganic substances, especially of silicates, at 25 °C. The temperature rise (0.15 °C) is measured with aid of a series of four pallaplat thermocouples, their voltage is registered with a mirror galvanometer. The energy equivalent of the calorimeter is measured by means of electric energy with error $\pm$ 0.02 %.

The calorimeter was tested in establishing the heat of solution of KCl. The standard deviation for single observations is $\pm$ 0.05 %.

In silicate chemistry reaction heats are either measured directly (e. g. high temperature calorimetry) or they are determined indirectly on the basis of the heats of solution. In the present paper we describe a calorimeter for determination of heats of solution of inorganic substances and especially of that of silicates.

The construction of the calorimeter had to be adapted to the sample size, to the exothermic character of the solution of silicates in the given solvents and to the corrosive action of the solvents used (HF, HNO_3 and others). The sample size (about 0.1 g) was predetermined by two conditions:

a) small amounts of samples prepared by quenching method, for which the calorimeter was made,

b) poor solubility of the specimen.

The temperature rise due to heat evolved in the reaction vessel is about 0.15 °C. In cases when the samples dissolve rapidly, the accuracy of calorimetric measurements is better than 0.1 %. The energy equivalent of the calorimeter is about 230 cal deg^{-1}. It is measured at about 25 °C. The thermal leakage modulus of the calorimeter is about 0.008 min^{-1}.

We took the solution calorimeter of H. E. Schwiete and A. Pranschke as a suitable model [1].

Experimental

Description of the Calorimeter

The design of the calorimeter is shown in Fig. 1.

Calorimeter Jacket

The jacket of the calorimeter is formed by a massive two-piece vessel with double walls made of polished sheets so that the water shield may be formed. Inside the vessel on a PVC support a Dewar vessel is placed *11* ($\varnothing = 11$ cm, height approx. 24 cm), its position is stabilized by means of rings of PVC *5* and silicone rubber *6*. The inside walls of the Dewar vessel are protected against the hydrogen fluoride vapours by a mixture of paraffine and polyethylene. The calorimeter lid consists of two parts:

a) of a copper cylinder *2* insulated from the other parts by felt packings *3*.

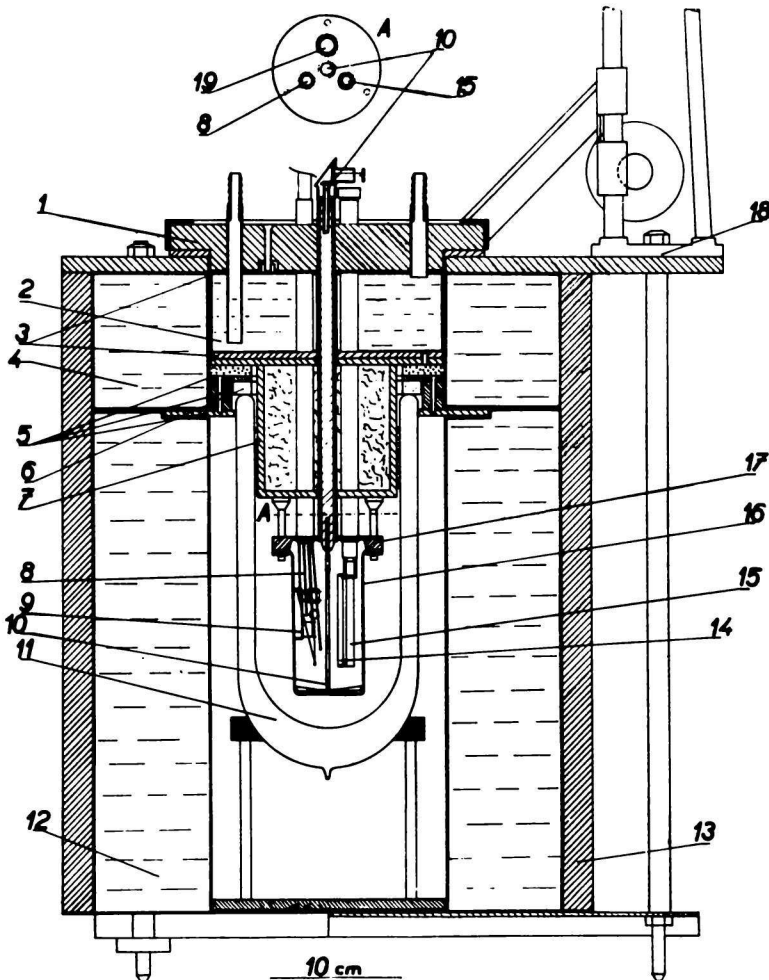*b*) of a PVC cylinder filled with crushed polystyrene. The hollow cylinder *4* and the

Fig. 1. Schematic diagram of the calorimeter.

jacket *12* form a continuous water shield whose temperature is held at 25 ± 0.001 °C. The calorimeter vessel *16* is placed in a Dewar flask in which the air is shut off by means of a felt packing piece placed at the outer wall of the cylinder *7*.

Tubes to stirrer, thermocouples, cooling and dropping devices are lead through the lid. The textgumoid plate *1* is connected with a cursor on the stand *18* so that the lid of the calorimeter may be shifted. The outside wall of the jacket is insulated with felt *13*.

Reaction Vessel with Accessories

The platinum reaction vessel *16* — capacity 250 ml with accessories — is covered by a teflon lid *17* and suspended on three PVC rods. The volume of the solvent is 225 ml. The weight of the solvent is determined with error ± 0.002 g. The stirrer *10*, the heater *14*, the cooling tube *15* and a series of four thermocouples *8* are submerged in the reaction vessel. A support for the sample container and for the breaking device is welded to the inner side of the vessel. All the above mentioned parts of reaction vessel are made of platinum or some precious metal. The bottom of the calorimeter vessel is asymmetrically concave so that no dead space should occur under the centre of the stirrer.

The platinum stirrer placed immediately over the bottom of the reaction vessel ressembles a propeller with six vanes. Over the liquid level the stirrer rod is interrupted by a thin-walled teflon tube which serves as thermal resistance [2]. The tilt angle of the vanes is about 20 °, one vane is tilted upwards to the axis of the stirrer so that turbulent flow of the liquid may occur. The stirrer is driven by a synchronic motor with 375 r.
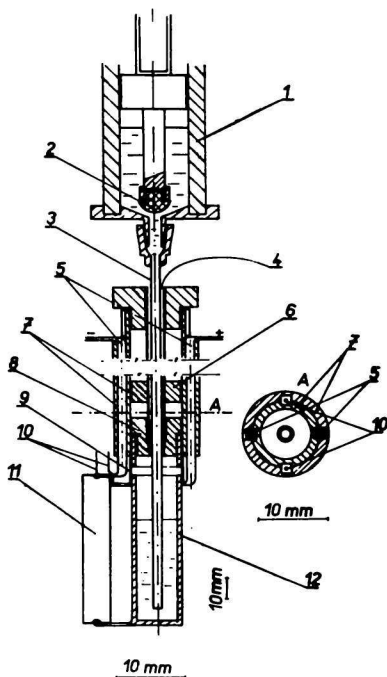

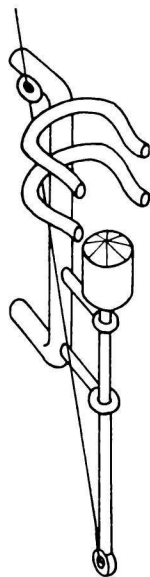*Fig. 2.* Cooling devise and heater.

Fig. 3. Support for the specimen container and the breaking device.

p. m.; with help of gears the stirring speed can be changed in a certain range. Heat input due to the stirring of the liquid is between 0.1—0.2 cal. min^{-1}.

The heater for calorimeter calibration by electric heating and the cooling assembly are shown in Fig. 2. The heater 11 is made of platinum-iridium wire ($\varnothing = 0.2$ mm) which is non-inductively wound on a teflon tube ($\varnothing = 4$ mm). A surface layer of paraffine and polyethylene protects the heater against the corrosive action of the solvent and inhibits the electrolysis. The current 5 and voltage 10 leads to the heater (Pt, $\varnothing_1 = 1$ mm, $\varnothing_2 = 0.3$ mm) are led in grooves between two PVC tubes 7. At 25.0 °C the resistance of the heater is $8.8252 \pm 0.0015 \ \Omega$. The temperature dependence of the electric resistance of the alloy PtIr$_{25}$ ($\beta \doteq 0.6 \cdot 10^{-3}$ deg^{-1}) with regard to the temperature rise used, does not manifest itself but within the error of the measurement.

The platinum tube 12 provided with thermal resistance 9 is a part of the cooling system of the calorimeter. This device serves to lowering of the temperature of the reaction vessel and of its content between solution and calibration runs to the starting temperature of the first period. The cooling is brought about by evaporation of ethylchloride. Prior to the cooling, the stop of the tube is taken away, the steel capillary 3 with the ring guide 6 is inserted into it and is forced into a cone mortise 8. Ethylchloride is dosed with an adjusted syringe 1, whose needle reaches as far as the bottom of the platinum tube 12. The upper opening of the needle is opened or shut with a rubber valve 2 placed on the prolonged piston. After the syringe has been filled with ethylchloride and the needle hole was opened, owing to the vapour pressure the ethylchloride is forced to pass to the bottom of the cooling tube. The vapours escape through a gap between the capillary and the needle 4. After cooling the syringe and the steel capillary are removed and the tube is sealed.

In case that the specimen under investigation does not react with the vapours of the solvent, its temperature is adjusted on the bottom of the dropping tube in a cylinder of pure cellulose (e. g. cigarette paper). The dropping device consists of two telescope PVC tubes. The outer fixed tube has a removable bottom. The inner tube with a bevelled lower part is mobile; pulling it out with help of a stranded wire, the bottom of the outer tube is opened and the sample container drops into the solvent. When the inner tube returns to its original position, the bottom is closed.

The second version of placing the sample in the calorimeter is shown in Fig. 3. The sample is put into a teflon cylinder ($\varnothing = 8$ mm, height 10 mm), which is closed on both ends by a thin membrane of polyethylene—paraffin mixture. When the sample has been put into the cylinder with soldered bottom, the lid is closed with a soldering torch. The sample container is then put into the sample holder. With a platinum punch which is set to movement by pulling a silon fibre, both membranes closing the two ends of the cylinder are torn off.

Temperature Measuring Assembly

Temperature in calorimeter is measured with four pallaplat thermocouples connected in series. One branch is made of PtRh$_{10}$ alloy and the second is made of the alloy Au$_{60}$Pd$_{30}$Pt$_{10}$. The EMF of the series is approx. 120 μV deg^{-1} at 25 °C, so that when the temperature rise is 0.15 °C, the measured voltage makes about 18 μV. When choosing the number of the thermocouples, we had to take into account the heat conduction of the wires which must not influence the required accuracy of measurement. With regard to low values of the investigated voltage, we recorded it with a sensitive two coils mirror galvanometer

(Kipp and Zoonen, type A 54). The current sensitivity is $1.2 \cdot 10^{-9}$ milliradian^{-1}, the inner resistance $R_1 = 50\ \Omega$ and $R_2 = 400\ \Omega$.

The above temperature measurement is advantageous as it yields a continuous temperature record in the course of the measurements with help of which we can:

1. follow the process of the solution,

2. estimate approx. the phase composition of the samples,

3. evaluate the correction for the heat exchange between the calorimeter and the surroundings in the main period.

The measuring junctions of the recording thermocouples are immersed in the solvent whereas the comparing junctions are kept at constant temperature $25 \pm 5 \cdot 10^{-5}\ °C$ in an ultrathermostat. The branches of the thermocouples are about 1.5 m long, the wire diameter is 0.5 mm and the total resistance of the series is $12\ \Omega$. The wire terminals reaching into the reaction vessel are protected by a layer of a mixture of polyethylene and paraffine. The spherical gold junctions ($\varnothing = 2$ mm) are bare and are placed in different heights in the reaction vessel so that they may record the average temperature. Comparing junctions of the thermocouples and the ends of the leads to the galvanometer are placed in a massive brass block (about 10 kg) with great heat capacity; the block is placed in the vessel of the Höppler ultrathermostat which also feeds the water shield of the calorimeter. The ultrathermostat has a heater with the input 10 W, it is cooled by water which is kept at temperature 0.3 °C lower than the temperature required (in order to keep the temperature variations as small as possible). The temperature of the brass block is read on the auxiliary mercury thermometer with 0.1 °C scale division. Two contact thermometers signal that the block temperature is in the allowed interval.

An essential lowering of the error of temperature measurement was brought about by a suitable arrangement of the galvanometer used in which there are two independent coils in the measurement system. The voltage of the temperature measuring thermocouples is lead to the 50 Ω coil, and when the main period has been terminated, a constant voltage of reverse polarity is lead from a series of four copper-constantan thermocouples to the 400 Ω coil. Thus, torsion moments of reverse sense acting on both coils are nearly compensated. Junctions of copper-constantan thermocouples are placed in the ultrathermostat whose temperature regulates the compensation voltage; the comparing junctions are in the ultrathermostat together with the comparing junctions of the measuring thermocouples.

The galvanometer works on the boundary of aperiodicity.

The electric leads to the galvanometer are provided with double iron shielding which is connected in one place. Three leads are conducted from the comparing junctions of the thermocouples (enamelled copper wire, $\varnothing \doteq 1$ mm). Two leads are connected with the galvanometer coil; the conductor which is lead out from the middle of the series of thermocouples is ground connected together with the shielding and with the galvanometer frame. The circuit is closed in such a way that two bare terminals of leads are put together and a non-isolated copper wire is wound round them in order to eliminate the switch interference.

We did not consider the simultaneous compensation measuring of the voltage of thermocouples; the required sensitivity of measurement is about $0.6 \cdot 10^{-8}$ V ($5 \cdot 10^{-5}\ °C$), whereas the sensitivity of available compensators is about 10^{-6} V.

As the continuous temperature recording with a galvanometer is advantageous, we did not think of measuring temperature with resistance thermometer.

The angle displacement of the galvanometer mirror in dependence on the temperature of the calorimeter vessel is registered with temperature recording system [3].

The calorimeter, the apparatuses and solvents whose temperature must be constant, are kept in a room where the temperature is maintained at 25.0 ± 0.2 °C.

The calorimeter is placed in a thermally insulated fume chamber (in order to remove hydrofluoride after the measurement) which is maintained at 25.0 ± 0.05 °C.

The instruments for temperature registration and those for calibration with electric current are placed in a separate room.

Calibration of the Calorimeter

The energy equivalent of the calorimeter is found by electrical calibration. The schematic diagram of the calibration circuit is in Fig. 4. A battery of lead accumulators supplies the electrical energy (12 V, 270 Ah). Further there is current stabilizer in the circuit with stabilization coefficient about $2 . 10^{-4}$ at 0.5 A. The ammeter A and the voltmeter V are used as indication instruments. With the relay (ZPA RP 90/220 V), controlled by the switch V_1, either the dummy resistor R_p with which the accumulators EMF are stabilised prior to the calibration run — or calibration circuit itself are connected to the circuit with battery. In the schematic diagram the relay contacts are given in rest position, the resistor R_p is switched in the circuit. When V_1 is switched on, the relay r_1 moves the contacts to the second position, the current passes through the
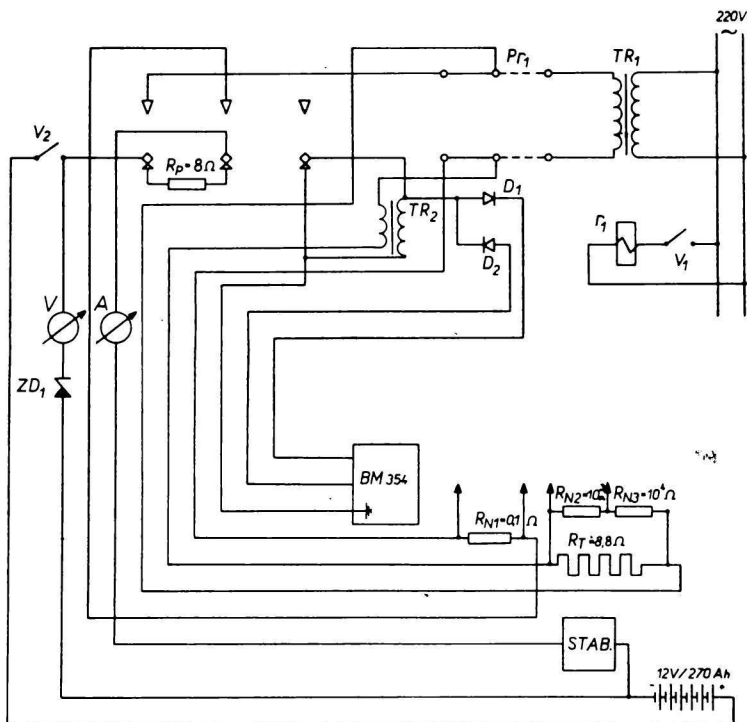

Fig. 4. Schematic diagram of the electric calibration circuit.

winding of the transformer TR_2, through the normal resistor R_{N1} and the heater R_T with the parallel distributor (R_{N2} and R_{N3}).

Passing of the current along the primary winding of the transformer TR_2 brings about a voltage impulse on its inductivity with help of which — after transformation and selection by means of diods D_1 and D_2 (Tesla 35 NP 70) — the gating circuit of the universal counter (Tesla BM 354) for precise time measuring is switched on. (For calculation of heats of solution, measurements of time in the range of 10^{-3} s are sufficient.) The gating unit of the counter is made in such a way lest it should not be sensitive to the vibrations of the contacts when the relays are switched.

The heating current is measured with the aid of a Dieselhorst compensator (VEB Messtechnik, Mellenbach) and the normal resistor R_{N1}. The voltage across the heater is measured with the aid of a resistance distributor (R_{N2} and R_{N3}), since with this compensator only voltages up to 1 V can be measured. The current strength is measured in the course of the calibration. The resistance of the heater is computed with help of the voltages and current strength recorded in the middle of the temperature interval in order to eliminate the influence of the temperature on R_T; for time-saving reasons these were measured after the calibration has been performed. When the calibration has been finished — when there is no more current in the circuit — a voltage impulse of reversed polarity is induced on the transformer TR_2 which closes the gating unit of the counter.

With help of an ultrathermostat, the normal resistor R_{N1} together with the current stabiliser and Weston cell of the compensator are kept in kerosene bath at the temperature 20.00 ± 0.02 °C.

With the switch P_{r1}, the transformer TR_1 can be directly connected to the heater in order to adjust the temperature of the reaction vessel to the desired value.

The error of the electrical calibration measurement is 0.02 %.

Measuring Procedure

When the thermal equilibrium in the calorimeter jacket and in the ultrathermostat with comparing junctions has been attained, the reaction vessel with the solvent, whose temperature has been adjusted, is closed in the calorimeter. In about two hours thermal equilibrium is established in the reaction vessel. The temperature rise is followed on the kymograf screen of the recording device. The finely ground sample (usually passed through a 0.04 mm sieve) is weighed on a microbalance with error $\pm 1 . 10^{-5}$ g and is put into the formerly mentioned teflon or paper cylinders.

After the starting temperature was adjusted to 24.95 °C (temperature record on the kymograf plate is a horizontal line) and after the stirrer and the recording device were started, the run may begin. The calorimetric curve is registered on the plate (Fig. 5).

In the initial period (10—15 min), the temperature change, due to heat of stirring and to heat exchange between calorimeter and surroundings, is approximatively linear.

In the main period (up to 5 minutes), the temperature rise due to the heat of the solution of the sample or to the heat evolved during the calibration run are measured. After the main period has been finished, the compensation voltage is connected to the 400 Ω galvanometer coil whereby the galvanometer deflection drops to value near zero and the galvanometer registers temperature change influenced by heat of stirring and by heat leakage between calorimeter and the surroundings (final period).

After every solution run the calorimeter is calibrated by electric heating. The conditions of both measurements are identical. Having finished the measurement of the heat of solution we allowed the reaction vessel to cool down with help of ethylchloride so

that it might attain the initial temperature in about one hour. For the calibration run, the time of heating is chosen in such a way that the height of both curves during the solution and calibration runs might be about identical.
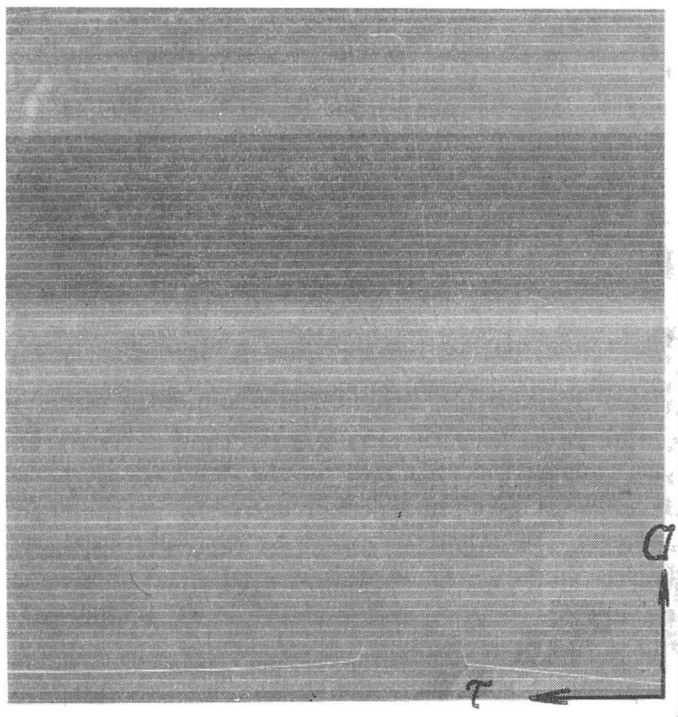

Fig. 5. Calorimetric curve.

Evaluation of Measurements and Analysis of Errors

Under adiabatic conditions, the heat of solution Q_s of the sample is calculated from the equation

$$Q_s = \frac{\Delta t_s}{\Delta t_e} \cdot Q_e.$$ (1)

Q_e is the heat evolved during the calibration by electric energy; Δt_s and Δt_e are the temperature rises in the course of the solution and calibration runs.

Assuming that in the temperature interval used ($\Delta t = 0.15$ °C), Δt is directly proportional to the angular displacement of the measuring unit of the galvanometer, we can write (1) as follows

$$Q_s = \frac{a + \Delta a}{a} \cdot Q_e = \alpha \cdot Q_e$$ (2)

where $(a + \Delta a)$ and a, respectively, are angular displacements of the measuring unit of the galvanometer (in terms of the scale division [3]) in solution and calibration runs.

Actually when the above method is used, the value of the coefficient α is distorted by the errors δ_i due to the heat exchange between the reaction vessel and its surroundings during the main period and further by errors in measurements of voltage changes by the deviation method ε_i.

The value of the error δ can be calculated for every temperature change from the equations (3) and (4) [4]:

$$\delta \doteq \left[\bar{v}_3 + \frac{\bar{v}_1 - \bar{v}_3}{\bar{t}_3 - \bar{t}_1} \cdot \left(\bar{t}_3 - \frac{\int t \mathrm{d}\tau}{\Delta \tau} \right) \right] \Delta \tau, \tag{3}$$

$$\delta = \left[\bar{v}_1 + \frac{\bar{v}_1 - \bar{v}_3}{\bar{t}_3 - \bar{t}_1} \cdot \left(\bar{t}_1 - \frac{\int t \mathrm{d}\tau}{\Delta \tau} \right) \right] \Delta \tau, \tag{4}$$

where $\bar{v}_1$ and $\bar{v}_3$ are, respectively, the average values of the rate of temperature rise in the reaction vessel in the first and in the third period; $\bar{t}_1$ and $\bar{t}_3$ are the average temperatures in these periods, $\Delta \tau$ the duration of the main period.

The quantities in (3) and (4) are read from the calorimetric curve and $\int t \mathrm{d}\tau$ is calculated from area under the curve representing the main period.

Let us design the error in the coefficient α, due to the errors ε_i, as ε_α; the following equation is valid for the dependence of ε_α on the values of ε_s in the solution run and ε_e in the calibration run:

$$\varepsilon_\alpha = \frac{a' + \Delta a' + \varepsilon_s}{a' + \varepsilon_e} - \frac{a' + \Delta a'}{a'} = \frac{a'(\varepsilon_s - \varepsilon_e)}{a'(a' + \varepsilon_e)} - \frac{\varepsilon_e \Delta a'}{a'(a' + \varepsilon_e)}, \tag{5}$$

where the prime values are corrected with regard to the error δ.

The error ε consists of following components:

a) a systematic error difficult to be determined which is due to mechanical properties of the measuring system of the galvanometer and to the inhomogenity of the magnetic field in which the coil is deflected. The absolute value of this error increases with the increasing deviation a',

b) random errors due to variability of mechanical properties of the galvanometer and to other circumstances.

With regard to random errors in the determination of α by the above method, $|\varepsilon_\alpha|$ can, according to (5), attain relatively high values even when $\Delta a' = 0$. This error is considerably lowered when the previously described method of measurement with two coils galvanometer is applied. When the current passes through both coils (after the main period has been finished), the galvanometer shows but a small deflection b with a small error ε_0 (Fig. 5). The initial deflection $(a' + \Delta a')$ in the solution run and a' in the calibration run

were both lowered by c, owing to the compensation by the constant voltage. The value of c for which we take the arithmetic mean of several values measured by the deflection method is afflicted by constant error ε in the numerator and in the denominator of the first term of the equation (6). Assuming that in the ideal case $\varepsilon_0 = 0$, then

$$\varepsilon_\alpha^0 = \frac{b + c + \Delta a' + \varepsilon}{b + c + \varepsilon} - \frac{b + c + \Delta a'}{b + c}. \tag{6}$$

If we substitute a' for $(b + c)$ in (6), we can calculate ε_α^0 with help of the compensation measurement of the deflections $(a' + \Delta a')$ and a' from the equation

$$\varepsilon_\alpha^0 = - \frac{\varepsilon \Delta a'}{a'(a' + \varepsilon)}. \tag{7}$$

From the comparison of (5) and (7) it follows that $\left| \varepsilon_\alpha^0 \right|$ always decreases, in contrast to $\left| \varepsilon_\alpha \right|$, with the decreasing value of $\left| \Delta a' \right|$. The values b and $\Delta a'$ equal about 1 % of a', so that the absolute values of errors ε_0 and ε_α^0 are small. As it is, the measurement approach the ideal case.

Testing of Precision and Acuracy

Precision of calorimetric measurement was verified by finding electrical energies related to the identical temperature rise: 31.214; 31.209; 31.167; 31.204; 31.207; 31.184; 31.192; 31.152; 31.209; 31.179; 31.177; 31.176. Arithmetic mean of this series of measurements is 31.189 ± 0.006 cal. The standard deviation for single observations is approx. ± 0.06 %.

The accuracy of measurements of the heats of solution with this apparatus was verified by establishing a series of values of heats of solution for KCl at 25 °C. Heat used for the solution of the specimen was immediately compensated by electric heating. In spite of this the temperature of the calorimeter vessel was not constant owing to the different heating rate and different rate of heat absorption in the course of the solution of KCl. As the starting of the electrical heating and its input were adjusted in such a way that the temperature deviations from the mean value might be nearly identical in both senses, the error due to the heat exchange (δ) could be neglected.

We found following values $(\Delta H_{25\ °C})_{KCl,\ sol.}$ [cal mol^{-1}] (dilution 0.073 mole KCl in 100 mole H_2O): 4178.7; 4176.0; 4182.3; 4177.0; 4179.3; 4175.6; 4180.6; 4178.3; 4177.9; 4176.7. The arithmetic mean $(\Delta H_{25\ °C})_{KCl,\ sol.} = 4178.2 \pm 0.6$ cal mole^{-1}.

Interpolating the values of heats of solution for KCl, as these were determined by E. Lange and J. Manheim [5] at 25 °C, we get for the given dilu-

tion $\Delta H_{KCl, sol.} = 4180.2$ cal mole^{-1}. The heat of solutions we found differs from the above value by 2 cal mole^{-1}, i. e. by 0.05 %.

KALORIMETER NA MERANIE ROZPÚŠŤACÍCH TEPIEL

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Opisuje sa kalorimeter na meranie rozpúšťacích tepiel anorganických látok, predovšetkým silikátov. Prístroj sa skonštruoval s ohľadom na malé návažky vzoriek, na ich obťažné rozpúšťanie a korozívne účinky rozpúšťadiel (HF, HNO$_3$ a i.). Meria sa pri teplote 25 °C. Tepelná kapacita kalorimetra je približne 230 cal deg^{-1}. Kalorimeter sa ciachuje elektrickou energiou s chybou 0,02 %. Vzostup teploty 0,15 °C sa meria sériou štyroch palaplatových termočlánkov pomocou citlivého zrkadlového galvanometra s dvoma cievkami (50 a 400 Ω). Na 50 Ω cievku sa privádza napätie termočlánkov merajúcich teplotu a na 400 Ω cievku sa po skončení hlavnej periódy privádza konštantné napätie opačnej polarity zo série štyroch termočlánkov med—konštantán. Torzné momenty pôsobiace na obidve cievky sa prakticky kompenzujú, takže konečná výchylka je malá. Týmto spôsobom sa podstatne znižuje chyba merania EMN termočlánkov galvanometrom výchylkovou metódou. Uhlová výchylka sa zaznamenáva registračným zariadením [3] s možnosťou odčítania 5 . 10^{-5} °C pre dané usporiadanie. Presnosť merania na kalorimetri sa overila nameraním hodnôt tepiel [cal], dodaných elektrickým ohrevom a vztiahnutých na rovnaký teplotný vzostup. Stredná kvadratická odchýlka jedného merania je približne 0,06 %. Správnosť merania rozpúšťacích tepiel sa overila sériou meraní rozpúšťacieho tepla KCl vo vode (zriedenie: 0,073 mólov KCl na 100 mólov H$_2$O) pri 25 °C. Hodnota aritmetického priemeru $\Delta H_{rozp.} = 4178,2 \pm 0,6$ cal mol^{-1}. Táto hodnota sa od údaju v literatúre [5] líši o 2 cal mol^{-1} (0,05 %).

КАЛОРИМЕТР ДЛЯ ИЗМЕРЕНИЯ ТЕПЛОТ РАСТВОРЕНИЯ

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Описывается калориметр для измерения теплот растворения неорганических веществ, главным образом силикатов. Прибор был сконструирован с учетом малых навесок образцов, их плохой растворимости и коррозийного воздействия растворителей (HF, HNO$_3$ и др.). Измерения производятся при 25°. Теплоёмкость калориметра равна, приблизительно, 230 *кал/град*. Калориметр калибруется электрической энергией с ошибкой 0,02%. Подъём температуры на 0,15° измеряется серией четырех палаплато-

вых термоэлементов с помощью чувствительного зеркального гальванометра с двумя катушками (50 Ω, 400 Ω). На 50 Ω катушку подается напряжение термоэлементов, измеряющих температуру, на 400 Ω катушку подается после окончания главного периода постоянное напряжение противоположной полярности из серии четырех термоэлементов медь—константан. Моменты вращения, действующие на обе катушки, практически компенсируются и поэтому конечное отклонение мало. Таким образом значительно понижается ошибка измерения ЭДС термоэлементов гальванометром методом отклонения. Угловое отклонение регистрируется прибором [3] с возможностью отсчета $5 \cdot 10^{-5}$ °С для данного оборудования. Точность измерения калориметра проверялась измерением значений теплот [кал], произведенных электрическим нагреванием и отнесенных к одинаковому температурному подъему. Среднеквадратическое отклонение одного измерения равно, приблизительно, 0,06 %. Справедливость измерения теплот растворения проверялась серией измерений теплоты растворения KCl в воде (разбавление 0,073 молей KCl на 100 молей H_2O) при 25°. Среднеарифметическое значение $\Delta H_{\text{раств.}} = 4178,2 \pm 0,6$ кал/моль. Это значение расходится с приведенным в литературе [5] на 2 кал/моль, что составляет 0,05 %.

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REFERENCES

1. Schwiete H. E., Pranschke A., *Zement* **24**, 593 (1935).
2. Sokolov V. A., Private Communication.
3. Proks I., Pach L., *Chem. zvesti* (in printing).
4. Rossini F. D. (Editor), *Experimental Thermochemistry*, 1, 32. Interscience Publishers, New York—London 1956.
5. Lange E., Manheim J., *Z. phys. Chem.* **150**, 349 (1930).

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