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COMPUTER-AIDED ACQUISITION AND PROCESSING OF DATA FOR CALORIC MEASUREMENTS WITH ISOPERIBOL CALORIMETERS

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SUMMARY

The undisturbed temperature equilibration of the vessel in an isoperibol calorimeter must follow an exponential time function. Any caloric effect within this vessel must cause a deviation of this function. A mathematical relation has been derived for linking the extent of this caloric effect and the integral of the temperature-time function.

This algorithm has been utilized for a computer program capable for an automatic acquisition of the data of an appropriate digital temperature meter and for the automatic calculation of the calorimetric results.

In two different calorimetric units these arrangements have been applied for the following determinations:

- specific heat capacities of liquid samples
- heats of chemical reactions
- reaction rates
- heats of vaporization of liquid samples.

INTRODUCTION

The aim of the present paper is to demonstrate the utilization of a computer for data acquisition and result evaluation in calorimetric measurements. The isoperibol calorimeter principle was chosen in view of the welldefined time dependence of its temperature equilibration.

DEFINITIONS

An isoperibol calorimeter is defined by the following conditions:

$$T(F) \neq f(t) \neq f(x) \tag{1}$$

$$T(M) = f(t) \neq f(x) \tag{2}$$

$$R(th) = f(x) \neq f(t) \tag{3}$$

where T(F) = Temperature of the furnace (surroundings)

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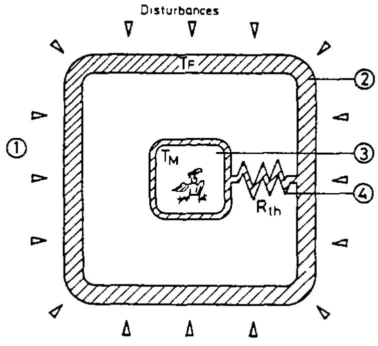
T(M) = Temperature of the measuring system

R(th) = Thermal resistance of the insulating layer between the inner calorimetric vessel and the isothermal surrounding furnace.

t = time

x = locus

All heat exchanges by radiation or convection have to be excluded.



Isothermal operation:
R_{th} Very small
$T_F = T_M =$ Constant

Adiabatic operation:
R_{th} Very large
$T_F = T_M$

Isoperibol operation:
R_{th} Defined
T_F Constant
$T_M = T_M(t)$

T_F	Temperature of furnace (surroundings)
T_M	Temperature of measuring system
R_{th}	Thermal resistance

① Environment, ② Furnace (surroundings), ③ Measuring system, ④ Thermal resistance

Schematic representation of a calorimeter.

fig. 1: Illustration showing the definition of an isoperibol calorimeter see lit. (1)

Conceptually this means that the temperature of the inner measuring calorimeter vessel is a function of time - but NOT of the local position on its surface. The temperature of the outer surrounding furnace is independent of time AND local position. The thermal resistance of the insulating layer is also independent of time - but it MAY exhibit local spatial differences. This point is essential in view of all inhomogeneities present in the isolating system as a whole. Even highly conductive components, such as wires and the metallic temperature measuring probes constitute parts of the entire isolating system. The overall heat conductivity is given by:

$$1/R(th) = 1/R(1) + 1/R(2) + 1/R(n) = f \qquad (4)$$

f = thermal conductivity coefficient.

FUNDAMENTALS

If the conditions (1) to (3) are satisfied, the caloric transport from the inner measuring vessel through the thermal resistance to the outer furnace is governed by the following equilibration equation:

$$\frac{d(T(M) - T(F))}{d\,t} = - f * \frac{A}{x} * \frac{(T(M) - T(F)}{m * cp} \qquad (5)$$

where: A = area of the insulating layer
x = thickness of the insulating layer
m * cp = heat capacity of the entire measuring vessel
f = coefficient of thermal conductivity for the entire insulating system (including metallic wires and so forth).

In this calorimeter only relatively small temperature variations occur, and thus the dependence of the specific heat capacity cp on temperature can be neglected. cp can therefore be combined with all the other constants mentioned above in a single constant K:

$$\frac{f * A}{x * m * cp} = K$$

Equation (5) simplifies to:

$$\frac{d(T(M)-T(F))}{d\,t} = - K * (T(M)-T(F)) \qquad (6)$$

Separation of the variables and integration yields:

$$\ln\,(T(M) - T(F)) = - K * t + C \qquad (7)$$

The integration constant C is given by the initial conditions at t = 0, i. e.:

$$\ln \left(\frac{(T(M) - T(F))}{(T(M) - T(F))o} \right) = - K * t \tag{8}$$

(T(M) - T(F))o refers to the difference between T(M) and T(F) at zero time.

The aim of the proposed computer-assisted evaluation is to provide this starting temperature difference as a general indication of all thermal effects in the isoperibol calorimeter. In simple applications, such as the determination of a specific heat capacity, this difference can be evaluated by a graphical extrapolation (see Hemminger-Hoehne, l. c. p. 97, fig. 2). On the other hand, this method is hardly applicable for systems with slow chemical reactions (see fig. 3). With such complications, extrapolation procedures become unsuitable, even if used in conjunction with computers. In such cases eq. (8) offers an alternative approach via integration:

From eq. (8) it follows that:

$$(T(M) - T(F)) = (T(M) - T(F))o * \exp(- K * t) \tag{9}$$

To explain this procedure, the following special case should first be considered: at large operation times for the isoperibol calorimeter T(M) is equal to T(F). In this special case T(F) could be compensated to zero and omitted in eq. (9). This case is comparable to that illustrated in fig. 2.

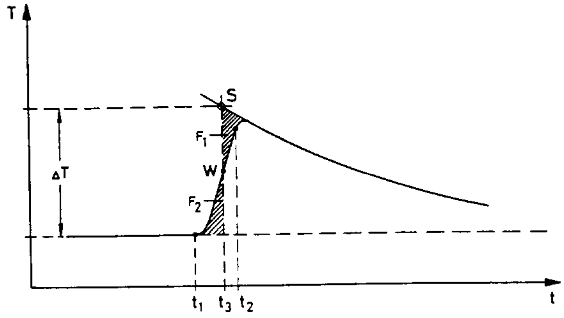
Eq. (9) simplifies to:

$$T(M) = T(M)o * \exp(- K * t) \tag{10}$$

By integration it follows that:

$$T(M) \;\; dt = - \frac{T(M)o}{K} * \exp(- K * t) + C \tag{11}$$

C = integration constant



T	Temperature
t	Time
t_1, t_2	Moments of the beginning and end of heat production
t_3	Moment of time when $F_1 = F_2$
ΔT	Reconstructed temperature increase of the system

Reconstruction of the "true" temperature increase in an "adiabatic" calorimeter with heat leakage.

fig. 2: Temperature evaluation by graphical extrapolation technique, see lit. (1)

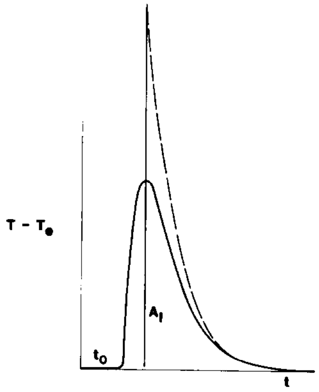


fig. 3: Theoretical extrapolation technique comparable to fig. 2 with a slower chemical reaction, see lit. (2)

The corresponding definite integral is:

$$\int_0^t T(M)\,dt = -\frac{T(M)(t(o))}{K} * (\exp(- K * t) - 1) = F(t) \qquad (12)$$

F(t) is the integral area of the T(M) - curve up to time t.

This is equal to:

$$T(M)(t(o)) = K * F(t) + T(M)(t) \tag{13}$$

T(M)(t) is the temperature of the inner calorimetric vessel at the moment (t) corresponding to the upper integration limit.

Since:

$$K = \ln \left(\frac{T(M)(n-1)}{T(M)(n)} \right), \tag{14}$$

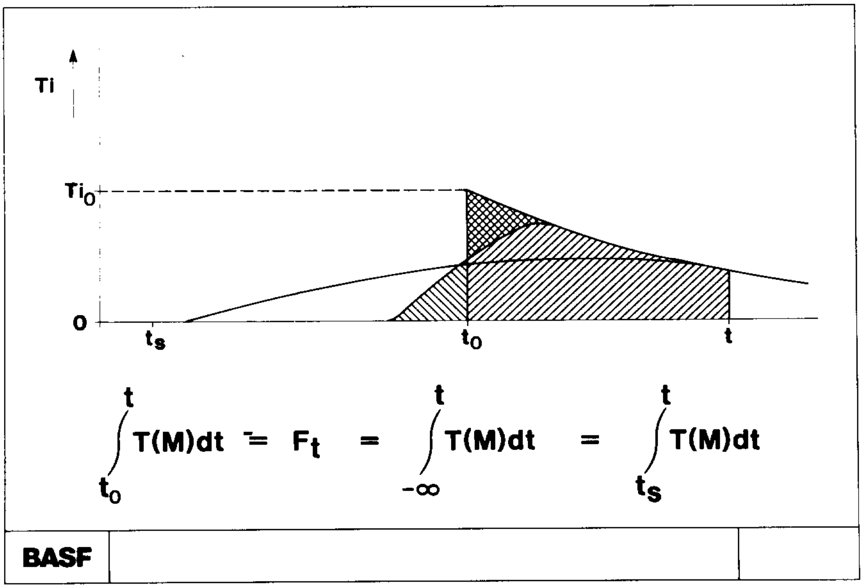
(n is the number of temperature data acquisition points at equal time intervals.)

it follows:

$$T(M)(t(o)) = T(M)(t) + F(t) * \ln \left(\frac{T(M)(n-1)}{T(M)(n)} \right). \tag{15}$$

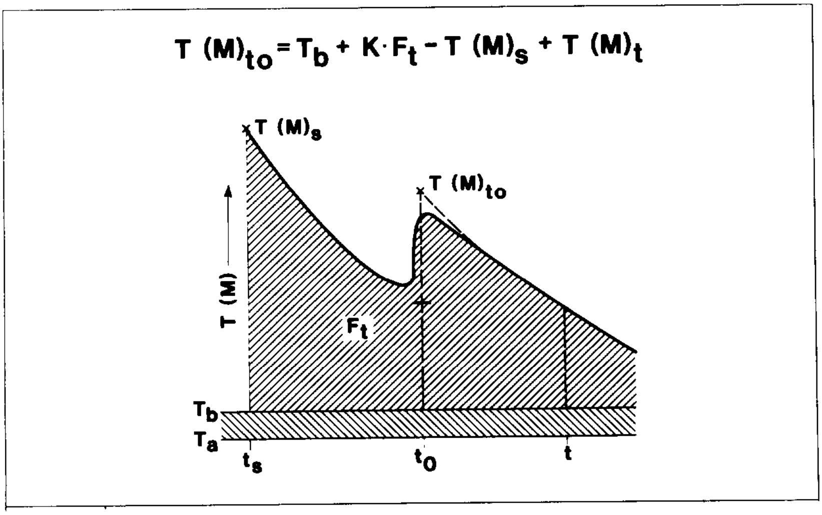
T(M)(t(o)) is the desired virtual temperature rise for the imaginary situation in which all caloric effects take place in one instantaneous event. This T(M)(to) is independent of t if (t) (the upper integration limit) lies on the exponential temperature decay trajectory, as K (eq. (14)) is constant. T(M)(to) is not dependent on an integration limit lower than t(o), since T(M)(t) is zero for t < to and the integration below this point makes no contribution to F(t). In other words, if the integration has been started before the caloric effect begins and carried through until its end, that is until the exponential decay function has been reached, eq.(15) yields the correct value for T(M)(t(o)). The fig. 4 shows the corresponding time function.

Eq. (15) has been derived under the assumption of a constant steady temperature in the calorimeter prior to measurement. Here the situation has been simplified by setting this temperature to zero. In fact this simplification can be overcome. Whatever value T(M) may have prior to measurement, the physical definition of the isoperibol calorimeter (eq. (1) - (3)) requires an exponential approach to T(F). For the additional caloric effect to be measured we have the addition of two distinct exponential functions with different starting points, but with exactly equal decay constant K, (see fig. 5).



$$\int_{t_0}^{t} T(M)dt = F_t = \int_{-\infty}^{t} T(M)dt = \int_{t_s}^{t} T(M)dt$$

fig. 4: Calculated T(M)- time curves in an isoperibol calorimeter for equal heat evolutions within various periods.



$$T(M)_{t0} = T_b + K \cdot F_t - T(M)_s + T(M)_t$$

fig. 5: Calculated T(M) - time curve in an isoperibol calorimeter for measurements starting at any temperature value.

It follows that

$$T(M)(to) = F(t) * \ln \left(\frac{T(M)(n-1)}{T(M)(n)} \right) - T(M)(ts) + T(M)(t) + T_b \qquad (16)$$

where

$T(M)(to)$ = temperature rise due to the virtual instantaneous caloric effect

$T(M)(ts)$ = measured temperature at the beginning of the integration of the temperature - time - curve.

$T(M)(t)$ = measured temperature at the upper integration limit, i.e. after termination of the caloric effect.

Here all T(M) - temperatures are differences to the so-called "basal temperature" T(b). This is not identical with the surrounding temperature T(F). The definition of the isoperibol calorimeter requires that there be a uniform temperature throughout the whole sample in the calorimetric vessel (see eq. (2)). This can be effected by a vigorous mechanical stirring. A constant stirring gives rise to a constant heat flux from the inner calorimetric vessel to the surroundings. The amount of heat per unit time depends on the viscosity of the liquid sample at the temperature chosen. Thus T(b) must be determined individually for each sample at each furnace temperature T(F). The basal temperature is approached exponentially, i.e. asymptotically. Exactly it will be reached theoretically at infinite times. So an experimental determination would be somewhat time-consuming.

A more practical method is to calculate T(b). The sum of a geometric progression in given by:

$$\sum_{1}^{n} (a^{1} + a^{2} + \dots a^{n}) = \frac{1 - a^{n}}{1 - a} \qquad (17)$$

If $a < 1$ and $n = \infty$ it follows for this now converging progression

$$\sum_{n=1}^{n=\infty} = \frac{1}{1 - a}$$

All (T(M)-Tb)- values determined after equal time intervals must form a converging geometric progression. The sum of it is the difference between the first T(M)-value and Tb. This is easily accessible by calculating

$$Tb = \frac{T(M)(1) * T(M)(3) - (T(M)(2)^2}{T(M)(1) - 2 * T(M)(2) + T(M)(3)} \quad (18)$$

With three T(M) - values determined after equal time intervals of 10 min a Tb-value is calculated automatically. This is a provisional value. Then T(M)(2) is converted to T(M)(1), T(M)(3) to T(M)(2) and a new T(3) value is determined. If both provisional values agree within a limit of 10 mK, their average is regarded as the reliable Tb-value for the further measurements. If these two proposals do not agree within this limit, that must be due to the not yet established isotherm conditions of the surroundings or to any disturbances from the power line. In this case the T(M) - subroutine has to be continued until an agreeable Tb-value occurs.

EXPERIMENTAL

The fig. 6 shows a sketch of the isoperibol calorimeter constructed in accordance with the above mentioned considerations. Unless otherwise indicated, the components are of glass. The outer temperature T(F) is regulated by a commercial thermostat (LAUDA KP20). The liquid from this unit is passed through the double-walls of a cylindrical vessel with an inner diameter of 50 mm. The necessary wall-temperature at the top (see definition in eq. (1)) is provided by a block of aluminum, heat losses to the surrounding air being restricted by an insulating cap. Vertical holes through this block are provided for the heating wires and a metallic temperature probe (Pt-100). The inner calorimeter vessel (100 ml) is equipped with an electric heater within a suitable quartz finger and a well for the temperature probe introduced from outside the block. The liquid sample is stirred vigorously by a magnetic rod connected to a perforated cylindrical teflon tube, the mechanism being driven by an external field.

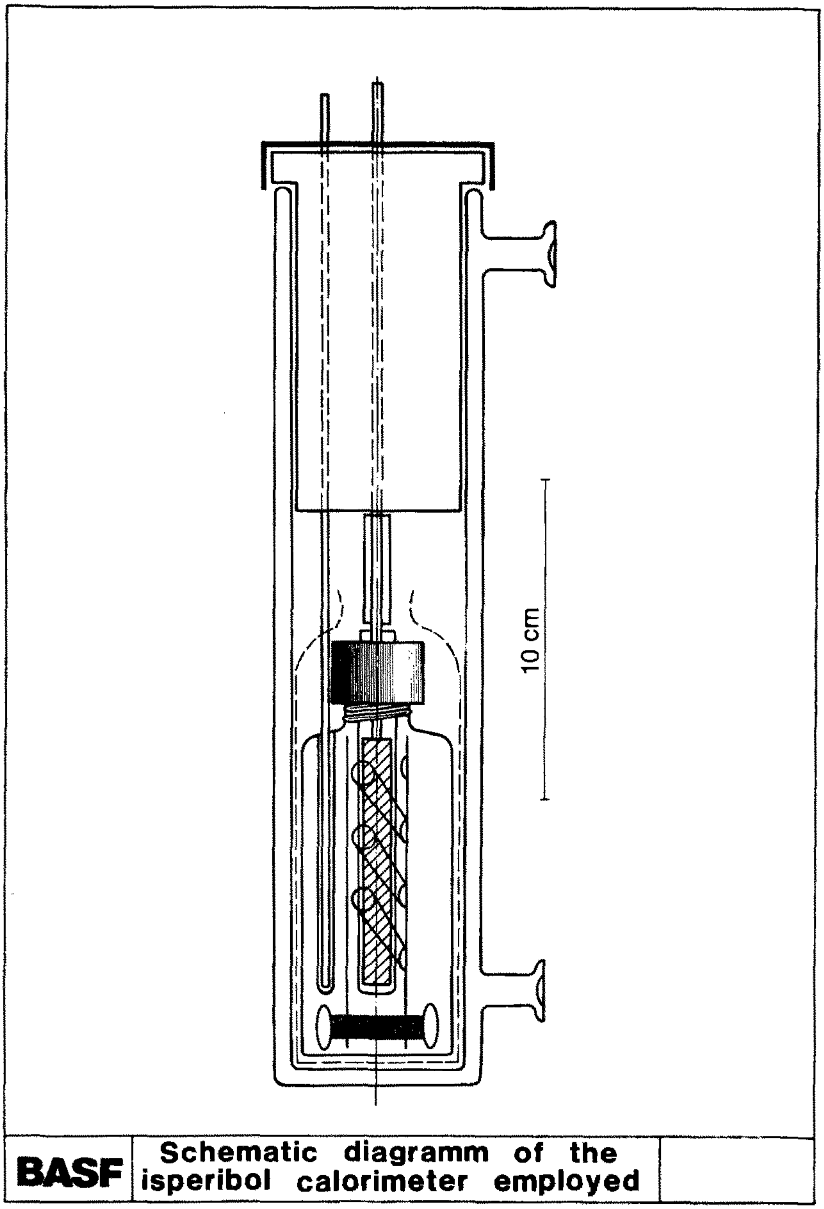


fig. 6: Schematic diagram of the isoperibol calorimeter employed.

In this way, even more viscous samples can be agitated adequately. The insulating layer indicated by a dotted line in fig. 6 consists of a cup-shaped cover of knitted wool. The temperature variation of the thermostat described is +/- 20 mK. The heat capacity of the inner vessel in conjunction with the insulating layer give the system a thermal inertia which is able to damp these unavoidable variations down to less than 1 mK (see table 1). Calorimetric measurements in the mK-region are thus feasible.

The digital temperature measurements are performed with Swedish "systemteknik"-thermometers for the range 0 and + 200 degrees C and with a repeatability of +/- 1 mK (see table 1). An electric pulse generator provides heating pulses with a regulated intensity and a digitally determined time interval. This is the experimental basis for measuring temperatures and comparing the results with those obtained after heating the calorimetric vessel with defined amounts of energy.

90.312	91.615
90.296	91.616
90.286	91.615
90.283	91.616
90.278	91.615
90.287	91.615
90.288	91.615
90.294	91.615
90.287	91.615
90.280	91.615
90.281	91.615
90.277	91.615
90.279	91.615
90.289	91.614
90.305	91.614
90.320	91.614
90.328	91.614
90.324	91.614
90.309	91.614
90.292	91.614
90.283	91.614
90.292	91.614
90.288	91.614
90.300	91.614
90.308	91.614
90.319	91.614
90.326	91.614
90.325	91.614
90.329	91.613
90.329	91.613
90.328	91.613
90.331	91.613
90.333	91.613
90.343	91.613
90.346	91.613

table 1: Digital temperature readings at time intervals of 10 seconds: T(F) (left) and T(M) (right).

THE PROGRAM

Eq. (5) to (17) have been derived purely theoretically. The reality of effective measurements is not quite this simple. The following practical limitations may be encountered:

- The temperature readings are limited to whole milli-degrees.
- Disturbances via power line equivalent to several milli-degrees may occur.

A suitable program has to contain special subroutines to average the results and to eliminate these disturbances.

The eq. (16) has been transformed into:

$$T(M)(t(o)) = \ln\left(\frac{1}{n} * \sum_{1}^{n} \frac{(T(M)-T(b))(n-1)}{(T(M)-T(b)(n)} * \sum_{1}^{n} (T(M)-T(b))(n) \right. -T(M)(st) + T(b) + T(M)(n) \qquad (19)$$

with: n = number of data readings
T(M) = temperature reading in the calorimeter vessel
T(b) = predetermined and automatically saved "basic temperature" (see eq. (18)).

T(M)(t(o)) = the desired temperature step.
T(M)(st) = temperature reading in the calorimeter vessel at starting the measurement (n = o)

The fig. 7 shows the values of the averaging groups for T(M)(t(o)) according to eq. (19) as a function of the time after the start of the measurement. These values become constant when the exponential decay (see fig. 4) has been reached. For the determination of this final value and filtering it from disturbances an iterative program has been used: Five averaging groups have been compared respectively. If the value of group 1 (see fig.7) equals to the average of the following four within a limit of +- 3 mK, this result is regarded as reliable. If this agreement is not achieved, this first group is discarded, the subsequent ones are moved down a place and a new fith one is collected. If any of these results suffered from a severe disturbance, it must progress all groups down to the first one, until it is rejected from this position. So the entire determination is more time-cosuming, but it gives a correct and reliable result.

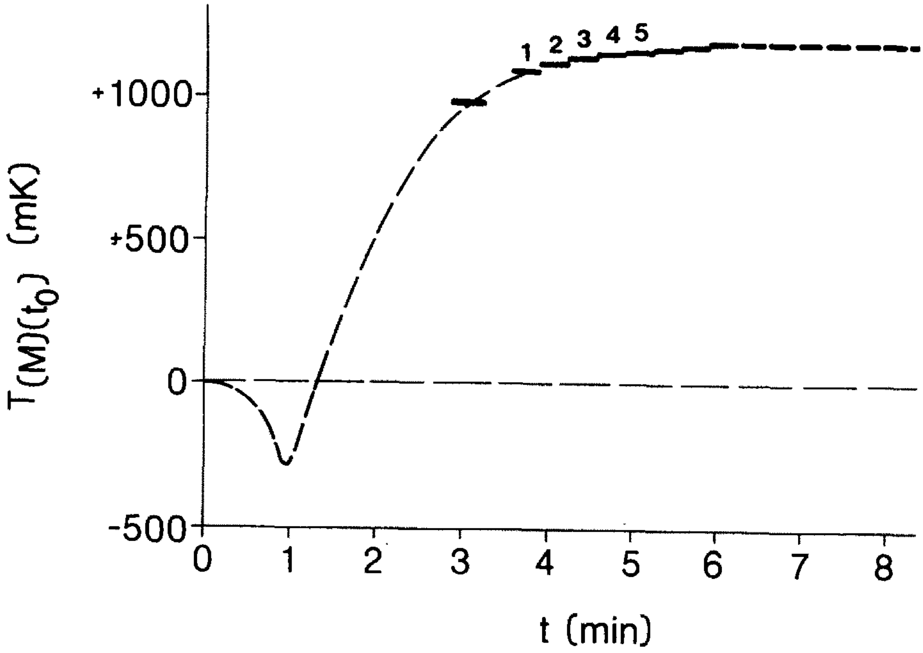


fig. 7: Averaging groups for T(M)(t(o)) according to eq. (19) as a function of time after having started the measurement.

CONTROLS

First, the exponential time dependence given in eq. (9) was checked. Over a temperature range of two decades, the variation in the K - values determined is less 1 percent. Secondly, the constancy of temperature jumps following similar electric heating pulses had to be confirmed. A constancy to within limits of +/- 2 mK was found using water as a standard. Water is a easily stirrable liquid with a specific heat capacity exhibiting only a slight temperature dependence between 30 and 100 deg. C. The constancy established (see table 2) indicates:

- The results for the desired temperature jumps are reproducible, regardless of temperature. The deviations are less than 2 mK.
- The electric pulses must similarly be reproducible.

This means that any temperature variations (e. g. due to chemical reaction can be accurately and conveniently determined and compared with those brought about by a reproducible and well-defined pulse heating.

```
Therm.Temp.=  70
I=         1.0000
          71.9950
I=         2.0000
          71.9324
I=         3.0000
          71.8859
        71.751599
I=         3.0000
          71.8513
        71.750698
Basistemp.=
          71.751
```

```
Probe Nr.    100
(Spiralzelle)
----------------
Probengewicht
[g]=       100.9
Heizleistung
[Joule]=   225.0
Messtemp.=
          72.048
Temp.Diff.=
           0.442
           =====

Heizleistung
[Joule]=   225.0
Messtemp.=
          72.402
Temp.Diff.=
           0.440
           =====

Heizleistung
[Joule]=   225.0
Messtemp.=
          72.671
Temp.Diff.=
           0.442
           =====

Heizleistung
[Joule]=   225.0
Messtemp.=
          72.836
Temp.Diff.=
           0.442
           =====

Heizleistung
[Joule]=   225.0
Messtemp.=
          72.908
Temp.Diff.=
           0.442
           =====

Heizleistung
[Joule]=   225.0
Messtemp.=
          72.942
Temp.Diff.=
           0.442
           =====
```

table 2: Reproducibility check for temperature jumps after similar electric heating pulses.

APPLICATIONS

1. Specific heat capacities

These determinations can be performed easily by relating the computed temperature jump differences to the energies of the respective heating pulses. Of course, a so-called "water value" (see "Calorimetry", l.c., page 15) has to be determined and stored in the program.

Although the energy indication from the electrical apparatus is probably reliable, it seemed preferable to have independent pulse energy measurements by the same calorimetric system. These were obtained in the following way: known quantities of two liquid samples with known specific heat capacities were heated consecutively in the same vessel by equal heating pulses. The specific heat capacities of these samples should be different. The following sample liquids were chosen:

water (cp see R. K. Freier: "Aqueous Solutions", Vol. 2 Supplements
Walter de Gruyter, Berlin, New York 1978)
(lit. (3))

n-heptane (cp see T. B. Douglas, G. T. Furukawa, R. E. McCoskey and
A. F. Ball, Journal of Research of the National Bureau of
Standards, Vol. 53, No. 3 Sept. 1954 Research Paper 2526)
(lit. (4))

It follows:

$$(m(1)*cp(1) + W) * T(M)(t(o))(1) = (m(2)*cp(2) + W) * T(M)(t(o))(2) \tag{20}$$

m(1) and m(2) = the masses of the samples

T(M)(t(o))(1) and (2) = the respective temperature jump differences.

W = "Water value", the heat capacity of the empty calorimeter vessel

$$W = \frac{m(1)*cp(1)*T(M)(t(o))(1) - m(2)*cp(2)*T(M)(t(o))(2)}{T(M)(t(o)(2) - T(M)(t(o))(1)} \tag{21}$$

With the programmed regression formula for the specific heat capacities of the above mentioned samples, the water value of the vessel and its temperature dependence could readily be calculated. The comparision of the respective pulse energy with the value given by the manufacturer gave identical values. This offers an additional confirmation of the correctness of the results.

Nearly all specific heat capacities normally encountered are between those of n-heptane and water. In light of the checks mentioned, all of the following results can be regarded as reliable.

The reproducibilities are normally < 0.5 % rel. - Table 3 shows a copy of the computer print-out table. In this output the temperature jump differences in [mK] have been also been printed.

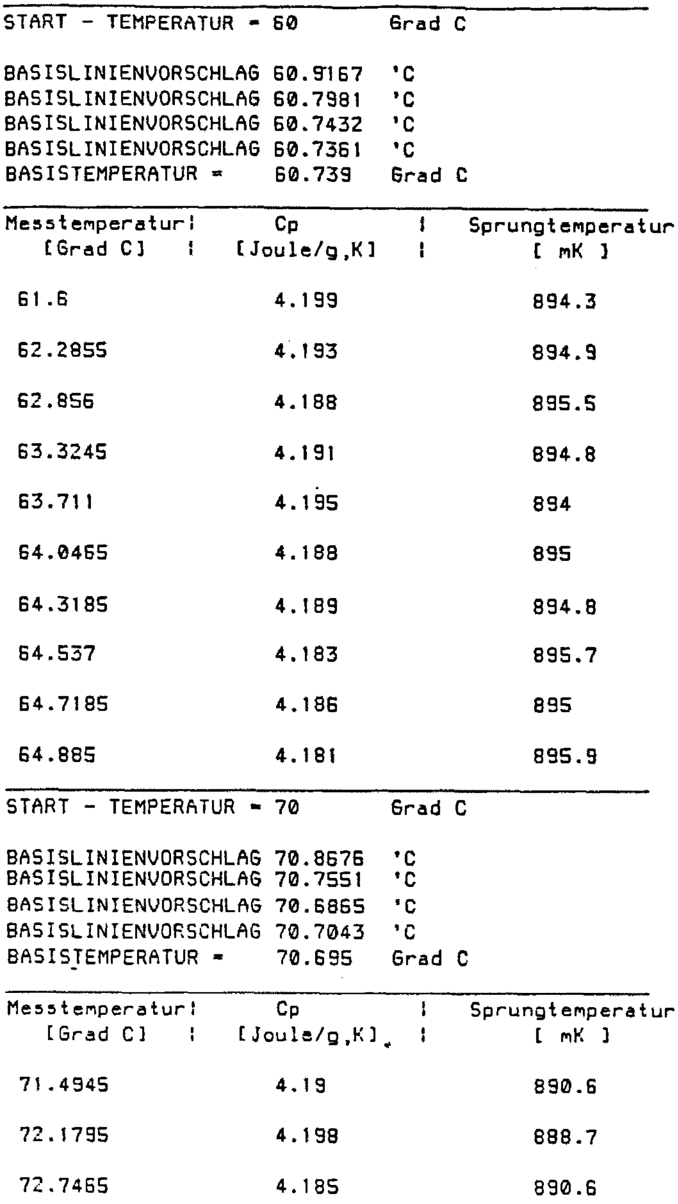
The calorimeter cell (see fig.6) is filled to approximately 95 % of its volume. The measured values actually are $c\sigma$ - values, taking into consideration the additional evaporation of the sample liquid into the remaining 5 % gas volume by the temperature raising of approximately 1 K. It can, on the other hand, easily be shown that the difference between $c\sigma$ and cp must be at least two decades smaller than the above given limit of reliability.

2. Heats of Reaction

The above-mentioned program based on eq. (19) operates in such a way that the T(M)(t(o)) - values of all averaging groups are calculated automatically. Five values are stored simultaneously. If the first agrees with the average of the following four to within a limit of 3 mK, the result is regarded as correct and the determination is terminated. If it does not agree, the first group is eliminated and the second one takes its place and so on as mentioned earlier. This loop can often run for quite a while before the results of five averaging groups are constant, i.e. just as long as heat is evolved or as long as the chemical reaction occurs.

Fig. 8 shows the calorimeter temperature as a function of time as recorded by an additional analogue recorder. Approximately 90 min. after the start, the computer finds the necessary agreement and gives a final value for the temperature jump. Subsequently four electric heat pulses follow for calibration purposes. - In this connection one should refer once again to fig. 3.

The result of this enthalpy determination must be correct, if the volume and viscosity changes accompanying the reaction are negligible. Otherwise separate calibrations are necessary.



```
START - TEMPERATUR = 60        Grad C

BASISLINIENVORSCHLAG 60.9167  'C
BASISLINIENVORSCHLAG 60.7981  'C
BASISLINIENVORSCHLAG 60.7432  'C
BASISLINIENVORSCHLAG 60.7361  'C
BASISTEMPERATUR =    60.739   Grad C

Messtemperatur!     Cp          !   Sprungtemperatur
  [Grad C]    !   [Joule/g,K]   !       [ mK ]

 61.6              4.199                894.3

 62.2855           4.193                894.9

 62.856            4.188                895.5

 63.3245           4.191                894.8

 63.711            4.195                894

 64.0465           4.188                895

 64.3185           4.189                894.8

 64.537            4.183                895.7

 64.7185           4.186                895

 64.885            4.181                895.9

START - TEMPERATUR = 70        Grad C

BASISLINIENVORSCHLAG 70.8676  'C
BASISLINIENVORSCHLAG 70.7551  'C
BASISLINIENVORSCHLAG 70.6865  'C
BASISLINIENVORSCHLAG 70.7043  'C
BASISTEMPERATUR =    70.695   Grad C

Messtemperatur!     Cp          !   Sprungtemperatur
  [Grad C]    !   [Joule/g,K]   !       [ mK ]

 71.4945           4.19                 890.6

 72.1795           4.198                888.7

 72.7465           4.185                890.6
```

table 3: Copy of an computer output listing with the specific heat capacities of water.

3. Reaction rates

In the cases considered previously, virtual temperature jumps have been determined as a measure of all caloric effects in the calorimeter vessel. After proper calibration with known heating pulses, the corresponding reaction enthalpy can be calculated exactly. This is normally what counts in calorimetric measurements.

However, information on the reaction rates can also be easily obtained with an isoperibol calorimeter. We begin with the question: what happens when no heat is evolved by the chemical system? The temperature of the calorimeter approches T(b) exponentially, according eq. (17) and (18). Calculated with regular time intervals these give (see eq. (14)):

$$K = \ln\left(\frac{T(M)(t)(n-1)) - Tb}{T(M)(t)(n) - Tb}\right)$$

If the temperature values observed obey the exponential law, K must be a constant. Deviations must be due to a heat-producing chemical reaction. This effect can be established by the difference to the later constant K - values.

For the additional measurement of the heat evolution as a function of time, one has to integrate eq. (19) with continuous registration of the K-values defined above. At the end of the caloric measurement this K - value attains a constant level which has to be substracted from the earlier registered K - values to obtain information on the heat evolution per unit time as a function of the reaction time.

On the other hand, these values are of only limited use for reaction kinetic calculations. According to eq. (2), the temperature of the calorimeter vessel must vary. In accordance with standard reaction kinetics, this influences the reaction rate considerably. Each individual case must be analyzed separately to see whether this effect is tolerable or not.

Heats of vaporization

Heats of vaporization are normally determined in two different ways:

1. Direct calorimetric measurement
2. Indirect calculation from the temperature dependence of the vapour pressures.

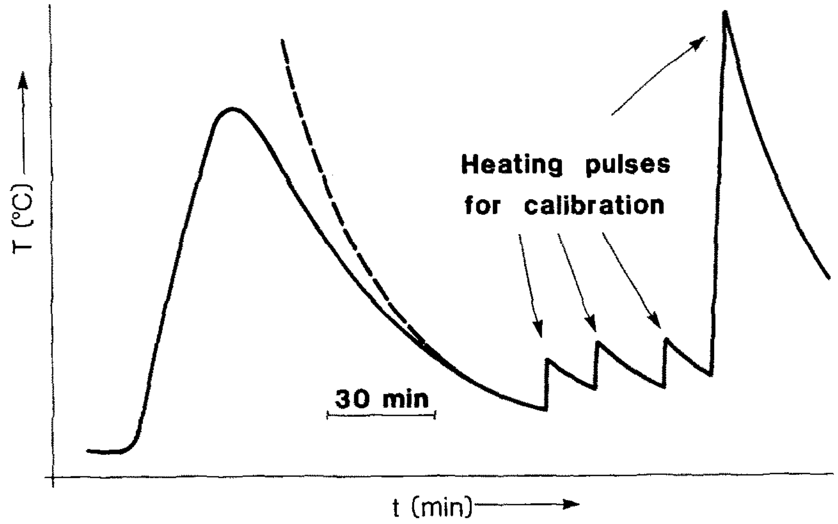


fig. 8: T(M) as function of time for a slow chemical reaction. This example is taken from a routine measurement in this laboratory.

The first technique has the advantage of greater reliability, but the disadvantage of the greater experimental effort. The second method is experimentally easier, but errors in the results may be severe (see V. Majer and V. Svoboda: "Enthalpies of Vaporization of Organic Compounds", IUPAC 1985, preface) (lit. (5)).

It would be useful to have an easy method for reliable calorimetric measurements of this quantity. The isoperibol calorimeter described here is naturally suited for the measurement of rapid caloric effects. A suitable calorimetric cell has been developed and is depicted in fig. 9. All the measurement and heating facilities are the same as in the cell shown in fig. 6. An inner vessel contains the liquid sample. This is connected by two small concentric teflon tubes (outer diameter of external tube: 3 mm) with an external inert gas circulation system. These teflon tubes are led out through tightly-fitting holes in the aluminum block. The outer vessel contains o-dichlorbenzene as a relative high boiling heat exchange liquid of relatively low viscosity. The heating finger and the temperature probe can also be seen. Both vessels are stirred magnetically by the same external field.

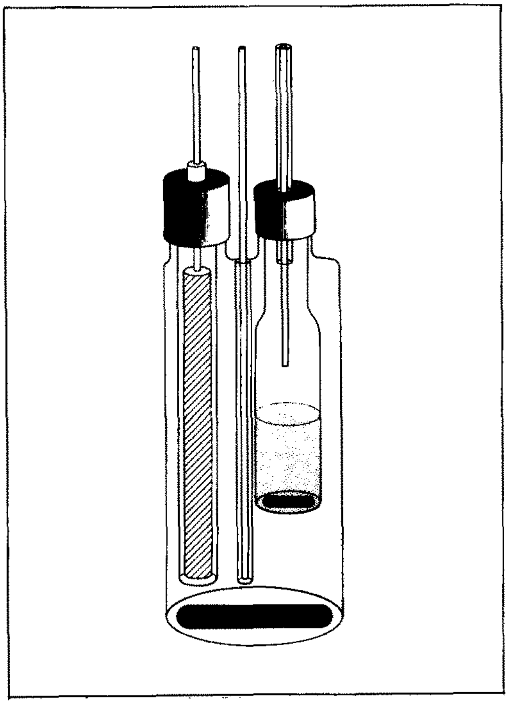


fig. 9: Calorimetric cell for the determination of heats of vaporization with liquid samples.

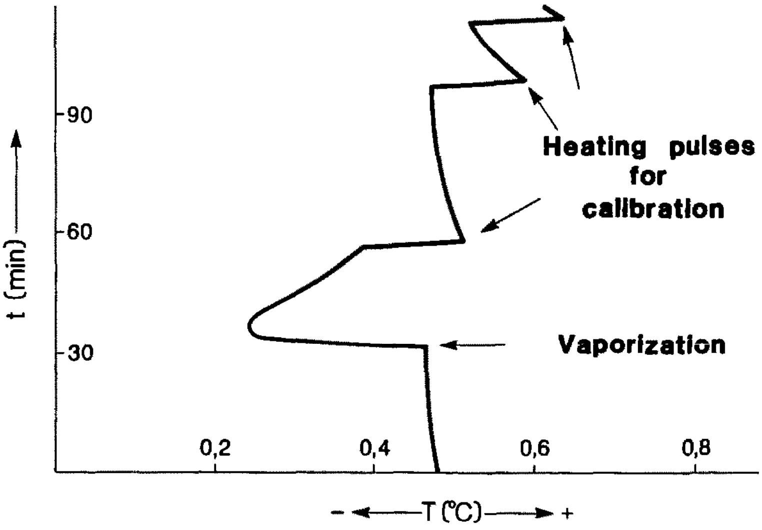


fig. 10: Recorder graph of the time-dependence of temperature in the cell of fig. 9 during determination of a heat of vaporization.

The measurement is performed at a temperature, at which the vapour pressure of the sample is approximately 100 mbar. Following temperature equlibration, part of the vapour-saturated air in the cell is slowly replaced with air. The quantity of the vapour is determined by weighing following absorption by a U-tube filled with active carbon in the gas circuit. After the vapour/air-exchange, the previous vapour concentration must be restored according to the prevailing temperature. The heat consumed during this vaporization lowers the temperature of the entire cell. This effect is measured and then compared with that obtained with a well-known calibration energy. Fig. 10 shows the corresponding temperature diagram.

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REFERENCES

lit. (1) W. Hemminger and W. Höhne: "Calorimetry", Verlag Chemie 1984 pp. 15,82,97
lit. (2) M.L. McGlasshan: "Current Trends in Precise Calorimetry" Thermochimica Acta, 72 (1984) 55 - 70
lit. (3) R.K. Freier: "Aqueous Solutions", Vol. 2 Suppl., Walter de Gruyter Berlin, New York 1978, p. 150.
lit. (4) T.B. Douglas, G.T. Furukawa, R.E. McCoskey and A.F. Ball: "Calorimetric Properties of Normal Heptane From 0 to 520 Deg.K" J. Res. Nat. Bur. Stand., vol. 53, No. 3, Sept. 1954 Research Paper 2526
lit. (5) V. Majer and V. Svoboda: "Enthalpies of Vaporization of Organic Compounds", IUPAC 1985 (Blackwell Scientific Publications), p. 9.