Thermodynamical Studies on Binary Systems Consisting of Polar and Non-polar Liquids. I. Construction of a Semi-automatic Microcalorimeter Suitable for the Rapid Measurement of Heats of Mixing of Binary Solutions

By Kazuo AMAYA*

(Received March 1, 1961)

For the full understanding of thermodynamical properties of binary systems, it seems to be very important to know about the relation between the termodynamical properties of binary systems and the structure of the constituent molecules.

The accumlation of this knowledge may contribute not only to the development of the theory of solutions but also to the application of it to practical purposes. To see how the dipole moment of polar molecules affects the thermodynamical properties of binary systems containing them, the measurements of heats of mixing for binary solutions consisting of polar and non-polar liquids were attempted.

The main obstacles which prevent the systematic study of heats of mixing for a large number of binary systems of non-electrolytes have been the difficulty, and the laboriousness, of the precise measurement of the small amount of heat evolved or absorbed on mixing two kinds of liquids of non-electrolytes.

Therefore, in designing a calorimeter the following points are taken into account.

1) Ease of the measurement, particularly the shortening of the time required for one measurement by an economical use of waiting time. It is essentially necessary to perform a large number of measurements in a short time.

2) Saving of the amounts of the samples required for each measurement.

3) Elimination of the errors due to evaporation or condensation of the components on mixing.

4) Durability for continuous operation of the thermostat for a long period.

By bearing the above points in mind, a semi-automatic microcalorimeter with the following features is constructed.

1) Five removable mixing vessels are attached to the calorimeter. They can be fitted to or removed from the calorimeter from the outside of the calorimeter chamber without seriously affecting its thermal equilibrium. This device cuts down the time required for the calorimeter to reach thermal equilibrium, after which the next measurement can be carried out, and hence is capable of shortening the waiting time required for each measurement.

2) An automatic measurement of the integrated time from 10^{-4} to 100 sec. during which the electrical current is passed through the calorimeter heater is carried out with an electronic counter, a gate circuit and a standard crystal oscillator.

3) An automatic thermal compensation is possible when the system is endothermic.

4) The quantities of samples required for each measurement are less than 1 cc. for each component.

5) The vapor phase is completely eliminated. This eliminates the error due to evaporation or condensation of the components.

Principle of the Construction of the Apparatus

The whole apparatus consists of a thermostat, a calorimeter, a thermister resistance thermometer, an automatic thermal compensation circuit composed the of constant current supply for the calorimeter heater and a relay circuit which exchange connection of a constant current supply from a dummy heater to the calorimeter heater, the automatic time measuring apparatus consisting of an electronic

* Present adress: Government Industrial Research Institute, Tokyo, Shibuya-ku, Tokyo.

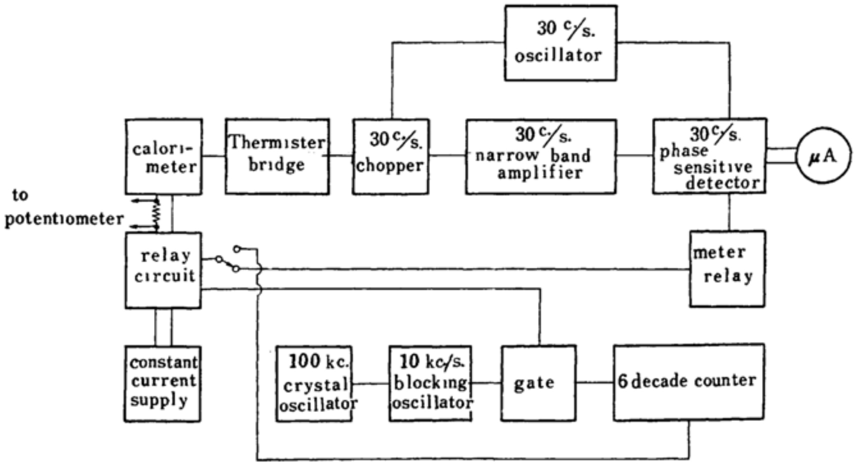

Fig. 1. Block diagram of the apparatus.

counter and the standard crystal oscillator and the gate, and a potentiometer for measuring the electric current of the calorimeter heater. The block diagram of the whole apparatus is shown in Fig. 1. The principle of the operation is as follows:

When the endothermic change occurs in the calorimeter, the signal from the thermometer is amplified by the vacuum tube amplifier and its output automatically operates the relay and changes the connection of the switch from the dummy heater to the calorimeter heater and supplies electrical energy to the calorimeter. At the same time, the gate circuit of the counter is opened and the signal of constant frequency of 10 kc. from a blocking oscillator synchronized by the 100 kc. crystal oscillator enters into the counter and begins to register the time. When sufficient energy has been supplied, the relay returns to its original position and ceases the supply of electrical energy to the calorimeter, and at that instance, the gate circuit is closed, and the integral value of the time during which the current is passed through the calorimeter heater is registered on the counter. For the part of the heat change which is not compensated perfectly, correction is made thereafter. For exothermic reaction, the change of temperature is plotted against time and the temperature change is referred to that caused by feeding a known amount of electrical energy.

The Details of the Apparatus

The Calorimeter. — The calorimeter consists of the mixing vessel holder rotatable around the horizontal axis, the removable mixing vessels, and the mixing vessel container. All of these are contained in the calorimeter chamber which consists of a liquid-tight

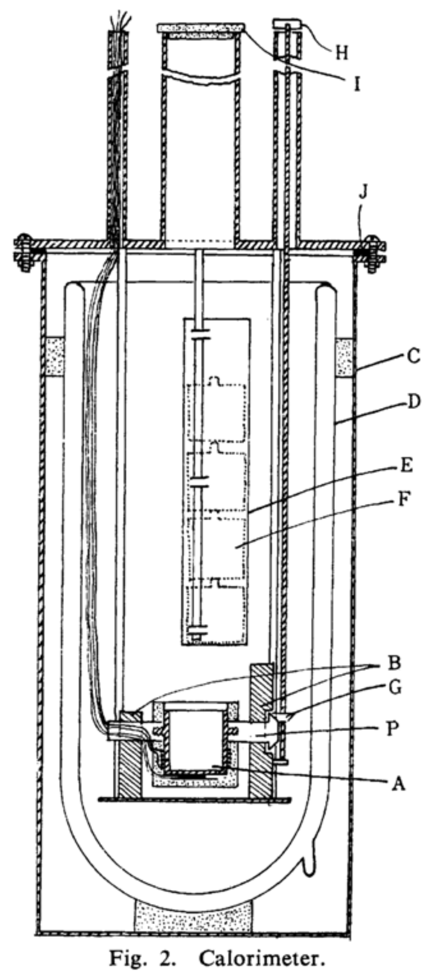

Fig. 2. Calorimeter.

A: Mixing vessel holder F: Mixing vessel
B: Bearing G: Bebel gear
C: Brass chamber H: Handle
D: Dewer vessel I: Lid
E: Mixing vessel container J: Rubber packing

cylindrical brass chamber with a large Dewer vessel in it. By this calorimeter a large number of measurements can be made without much labor. The calorimeter from which the mixing vessel is taken away is shown in Fig. 2.

Inside the holder, the removable mixing vessel is just fitted. This can be placed or removed the by use of a long bakelite rod. The mixing procedure is to make the holder upside down by turning it around the pivot P through the manipulation of the handle from the outside of the calorimeter chamber.

The Mixing Vessel Holder. — The mixing vessel holder is shown in Fig. 3. A is the

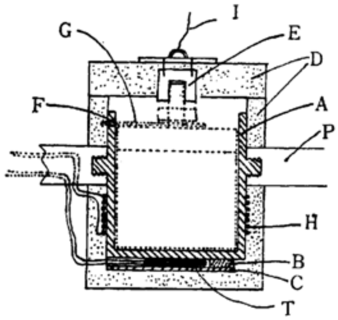

Fig. 3. Mixing vessel holder.

A: Brass vessel
B: Spacer
C: Copper plate
D: Foam styrene
E: Rubber cap
F: Small hole
G: Iron pin
H: Heater
I: String
P: Bakelite pivot
T: Thermister

mixing vessel holder made of a brass cylinder closed at one end and equipped with the pivot P. The cylinder is 3 cm. in inner diameter, 3.4 cm. in outer diameter, and 3.3 cm. in height. Around the outside wall of the cylinder, the calorimeter heater H of double silk covered manganin wire was wound non-inductively, and was fixed by Araldite resin. The resistance of the manganin wire is 45.850 Ω. The outside of the bottom wall of the mixing vessel holder is equipped with a thermister T of about 100 kΩ in resistance at 25°C. The thermister is enclosed in a thin polyvinyl chloride tube and sandwiched between the bottom of the holder and the cupper plate with a brass plate spacer of 2 mm. thickness with a slot, into which the thermister is just fitted, in order that the thermister may not be crushed. The pivot P, made of bakelite for thermal insulation, is fixed to the holder by a male screw extruding from the wall of the holder.

The pivot P is held by a bearing. The holder can be rotated around the pivot P through a bebel gear by rotating the pivot P with the handle outside the calorimeter chamber.

The leads of the thermister and the calorimeter heater are passed through the small holes bored along the axis of the pivot P and are drawn from the one end of the pivot P in order not to be entangled by the turning over of the holder.

The outside of the holder is all covered by foam styrene for thermal insulation.

The Container for the Mixing Vessels. — In a large space of the Dewer vessel, there is the mixing vessel container E which can contain four mixing vessels. The five mixing vessels filled with liquid samples to be mixed, are introduced into the calorimeter at one time. One of the five is held in the mixing vessel holder, and the other four are held in the mixing vessel container. When one measurement is finished, the mixing vessel in the holder is taken out of the calorimeter chamber and the one in the container is placed into the mixing vessel holder within the calorimeter chamber by the long bakelite rod without affecting the thermal equilibrium inside it.

The Mixing Vessel. — The mixing vessel is shown in Fig. 4. The mixing vessel consists

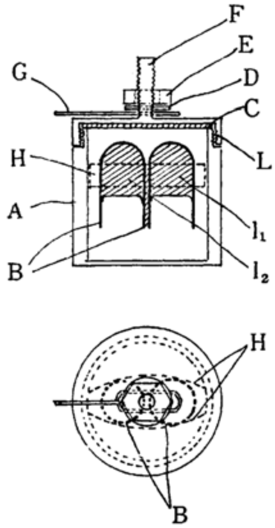

Fig. 4. Cross section and upper side view of the mixing vessel.

A: Iron vessel
B: Glass bells
C: Polyethylene sheet
D: Washer
E: Nut
F: Male screw
G: Iron pin
H: Spring steel plates
l_1, l_2: Liquid 1 and 2

of an iron vessel A and a lid L which are tightly fitted to each other by a screw, and two glass bells B fixed together by araldite resin. To make the vessel liquid-tight, a round sheet of polyethylene packing, 0.3 mm. in thickness, is placed between the vessel and the

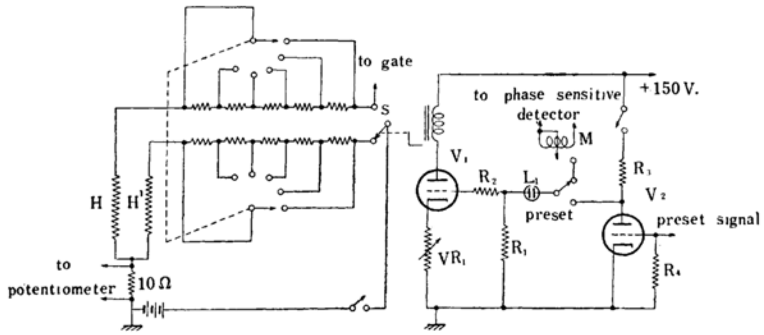

Fig. 5. Electrical circuit of automatic thermal compensation.

R_1: 1 MΩ	R_4: 100 KΩ	S: Micro switch	L: Neon lamp
R_2: 1 MΩ	VR_1: 3 KΩ	H: Calorimeter heater	V_1: 1/2 6SN7
R_3: 100 KΩ	M: Meter relay	H': Dummy heater	V_2: TY66G

lid. The mixing vessel is a cylindrical iron vessel 2.6 cm. in inner diameter, 3.2 cm. in outer diameter and 3.1 cm. in height. The vessel is filled with mercury and then the two kinds of liquid to be mixed are introduced into two glass bells by two syringes, one for each liquid; therefore they are confined above the mercury separately.

To prevent the bells from being raised above the surface of the mercury by bouyancy when the liquids are introduced into them, two spring steel plates the length of each being a little longer than the inner diameter of the iron vessel, are stuck to the inner wall of the vessel by their restoring force across the diameter of the vessel and the bells are clamped by them.

The syringe used in introducing the liquid into the bell is the usual one modified by attaching a screw driver and by bending the end of the needle.

The upper side of the lid is equipped with a male screw and a nut.

The male screw is used when the mixing vessel is placed into, or is removed from the holder from the outside of the calorimeter chamber by the long bakelite rod, at the one end of which there is a female screw just fitted to the male screw. The nut clamps the iron pin which prevents the mixing vessel from falling down out of the holder when it is turned upside down.

Through the upper part of the wall of the holder a small hole is bored, into which the pin at the upper side of the mixing vessel is put (see Fig. 3).

Before placing the mixing vessel into the holder, the iron pin is loosely held between the nut and the upper side of the lid. When the vessel is put into the holder, the end of the pin is guided into the hole above mentioned by a small piece of permanent magnet, held at the other end of the long bakelite rod described above, and then the nut is screwed by a nut driver from the outside of the calorimeter chamber. After these procedures have been finished, the upper side of the mixing vessel is covered with a foam-stylene lid. The lid is fixed to the mixing vessel by fitting a rubber cap put at the center of the lid to the top of the male screw attached to the lid of the mixing vessel. The rubber cap prevents the foam styrene lid from falling off when the vessel holder is turned. Thus all sides of the calorimeter are covered by foam styrene, and good thermal insulation is assured. The inside of the calorimeter chamber can be illuminated by a miniature lamp in order that these procedures can be performed with ease.

The Thermometer.—The thermometer bridge, the converter and the thermister resistance thermometer are the same as those described in the previous paper[1]. The amplifier is also similar to that previously described except that the first stage vacuum tube 6SH7 is replaced by 12AT7 tube in which the two triode plate load resistors are wire wound resistors of 100 kΩ. By the use of the wire wound resister as the plate load, the excess noise is reduced and the signal to noise ratio is raised about three times higher than before.

The Electrical Circuit for the Automatic Thermal Compensation. — The electrical circuit for the automatic thermal compensation consists of the constant current supply, the dummy heater, the calorimeter heater, and the relay which converts the connection of the constant current supply from the dummy heater to the calorimeter heater by a lowering of the temperature of the calorimeter.

The electrical circuit is shown in Fig. 5.

The output of the phase sensitive detector

1) K. Amaya and R. Fujishiro, This Bulletin, 29, 270 (1956).

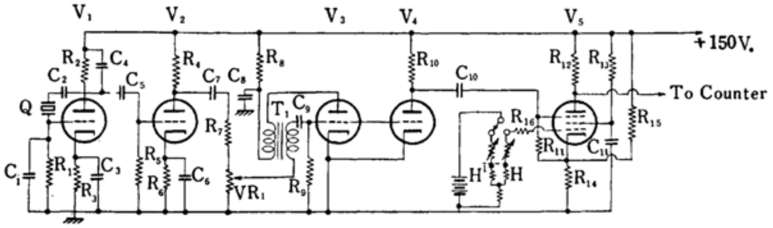

Fig. 6. The electrical circuit of the oscillator and the gate.

R_1:	100 kΩ	R_9:	150 kΩ	C_1:	250 pF	C_9:	250 pF	VR_1:	3 kΩ
R_2:	20 kΩ	R_{10}:	50 kΩ	C_2:	0.01 μF	C_{10}:	0.001 μF	H:	Calorimeter heater
R_3:	1 kΩ	R_{11}:	100 kΩ	C_4:	0.1 μF	C_{11}:	0.1 μF	H′:	Dummy heater
R_4:	20 kΩ	R_{12}:	100 kΩ	C_3:	250 pF	C_{12}:	0.001 μF	T_1:	Blocking trans
R_5:	500 kΩ	R_{13}:	150 kΩ	C_5:	250 pF	V_1, V_2:	1/2·5692		
R_6:	1 kΩ	R_{14}:	1 kΩ	C_6:	0.1 μF	V_3, V_4:	1/2·6SN7		
R_7:	30 kΩ	R_{15}:	20 kΩ	C_7:	250 pF	V_5:	6AS6		
R_8:	50 kΩ	R_{16}:	100 kΩ	C_8:	1 μF	Q:	100 kc. crystal		

of the thermometer amplifier is fed to a meter relay with sensitivity of 200 μA. When the needle of the meter relay touches the one contact point, the grid of the 1/2·6SN7 tube is connected to high potential through a neon discharge tube and the increased plate current operates the microswitch B and changes the path of electric current from the dummy heater to the calorimeter heater. This operation occurs when the temperature of the calorimeter changes by about 10^{-4}°C.

A standard 10 Ω resistor is connected in a series with both the dummy and the calorimeter heater. The current which passes through the calorimeter heater is obtained by measuring the electric potential across the 10 Ω standard resistor with the potentiometer. The constant current supply is a heavy duty battery of 6 V. terminal voltage.

The terminal of the microswitch which is connected to the calorimeter heater has a lead to the grid of the gate tube, and when the switch operates, the potential of 6 V. is applied to the grid of the gate tube. R and R' are pairs of resistors having the same resistance and are connected in series with the calorimeter and the dummy heater respectively. By changing the position of the arm of the rotary switch, the total resistance of R and R' is changed, with the resistance kept equal to each other and thereby the current is adjusted from about 15 mA to 120 mA in five steps.

The dummy heater is the resistor having an almost equal value of resistance to the calorimeter heater. Before starting the experiment, the current is passed through the dummy heater and the battery is made to be at a steady state. By the operation of the switch, the total load is nearly the same and the steady state is not disturbed.

The Time Measuring Apparatus.—It consists of the standard 10 kc. oscillator with the gate circuit and the six decade electronic counter. The electrical circuits of the former is shown in Fig. 6.

The standard 10 kc. oscillator is a blocking oscillator synchronized by the standard 100 kc. crystal oscillator. The frequency of the 100 kc. crystal oscillator is not corrected by the standard frequency. The gate tube is a 6AS6 tube. The 10 kc. signals from the blocking oscillator are fed to the third grid of the 6AS6 tube. When no voltage is applied to the first grid of 6AS6, a 10 kc. signal sufficiently large to operate the counter is not produced across the plate load resistor of the 6AS6 tube. But, when the gate signal of 6 V. is applied to the first grid of 6AS6, the 10 kc. signal, sufficiently large to operate the counter, comes out. This operation follows in an instant when the electric current from the constant current supply is passed through the calorimeter heater, and so there occurs no delay. By this electronic device, the errors otherwise introduced, of individual persons caused by delay of pushing stop watches or a delay caused by the mechanical inertia of electromagnetic switches, are completely eliminated.

The six decade electronic counter is made of six discharge tube type decatrons of multioutput type manufactured by Japan Radio Communication Co. For the first stage a single pulse decatron is used which responds to signals of up to 20 kc./sec., and the other five are the double pulse decatrons which respond only to signals of up to 5 kc./sec.

By this counter the integral time from 10^{-4} to 100 sec. can be measured with an error of $\pm 10^{-4}$ sec. multiplied by the number of operations of the gate circuit.

The counter is also able to pass electrical current through the calorimeter heater for a pre-determined time from 0 to 100 sec. in steps of 10^{-2} sec. But between the actual time and that pre-determined there is a difference of 3×10^{-2} sec. due to the mechanical inertia of the mechanical switch system.

The device stated above is convenient for supplying a known amount of electrical energy to the calorimeter.

The Thermostat. — The thermostat and the regulator are practically the same as those described previously. The only improvement is the replacement of the leather belt-pulley type stirrer with the V-belt gear driven one by which the continuous operation for about three months was made possible.

The temperature of the thermostat was kept constant within 10^{-4}°C at 25±0.1°C.

Procedures

Filling of the Bells with the Samples. — The mixing vessel with two glass bells in it is immersed into a pool of mercury and is turned two or three times in order to exclude the air in the bells and fill them completely with mercury.

Making sure that no air remains in the bells, the two kinds of liquid to be mixed are introduced into each of the two bells by two syringes one for each component.

The quantity of the liquid introduced is determined by weighing the difference of the weight of the syringe by a chemical balance to 0.5 mg. before and after introducing the liquids into the bells.

After the liquids are introduced into the bells, mercury is poured into the vessel until the mercury overflows the edge of the mixing vessel.

Then the round sheet of polyethylene, the size of which is sufficient to cover the whole cross section of the mixing vessel, is placed over the surface of the mercury in the mixing vessel. Making sure that no air exists between mercury and the sheet of polyethylene, the lid of the mixing vessel is put on it and is tightly screwed.

Similar procedures are carried out for the other four mixing vessels containing the same kinds of liquid but of different ratios. The amount of the liquids taken is so chosen that the concentration of the resultant mixture is made about 10, 30, 50, 70 and 90% in voluo.

The Measurement of the Temperature Change on Mixing.—The five mixing vessels filled with the sample are introduced into the calorimeter chamber, which is immersed into the thermostat, and one of the five into the mixing vessel container. Then the end of a pin on the lid of the mixing vessel placed in the mixing vessel holder is guided to the hole of the mixing vessel holder and tightly clamped. Then the foam styrene lid is fixed over it. They are then left over night.

After thermal equilibrium is attained, the resistance of the thermister is read every minute and then the liquids are mixed. The mixing is performed by rotating the mixing vessel holder by 180°C, and then by rocking it within a small angle for several times with the handle, from the outside of the calorimeter chamber. Before mixing, the battery for the constant current supply to the calorimeter heater is connected to the dummy heater in order to keep it in a steady state.

When the heat of mixing is endothermic, the thermal compensation takes place automatically. In this case the current passes through the calorimeter heater intermittently from two to four times according to the rate of heat evolution and to the magnitude of electric current passed, until the heat absorbed is nearely compensated for. Then the operation of the automatic thermal compensation circuit is stopped and the resistance of the thermister is read every minute for 15 to 20 min. by manually adjusting the resistance box of the thermometer bridge so as to make the output of the phase sensitive detector null.

The current which has passed through the calorimeter heater is measured to a fraction of second desimals of mA within the interval during which the thermal compensation operates and the current is passed through the calorimeter heater.

The integrated time during which the current is passed through is automatically registered on the electronic counter. Then the known small amount of electrical energy is supplied to the calorimeter to evaluate the part of the heat not perfectly compensated. And again the values of resistance are read for 15 to 20 min. to construct a resistance-time curve.

When the heat of mixing is exothermic, automatic thermal compensation is impossible. In this case the resistance of the thermister is read for 15 to 20 min. after mixing and the resistance-time curve is constructed. Then again a known amount of electrical energy which is nearly equal to the heat evolved on mixing is supplied to the calorimeter and the resistance-time curve is constructed in a way similar to what was done before.

Calculation of the Heats Evolved or Absorbed by the Use of Resistance-time Curves.—Typical plots of resistance versus time for endothermic heat of mixing with automatic thermal compensation are shown in Fig. 7.

Within the intervals during which the automatic thermal compensation circuit is in

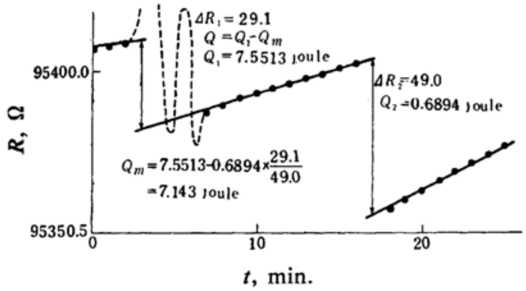

Fig. 7. Typical resistance vs. time curve for endothermic heat of mixing with automatic thermal compensation.

operation, the resistance of the thermister cannot be measured. The dotted line in the figure shows the plot that would be expected if it were actually made.

As the plots of resistance versus time after the thermal compensation ceases to operate are almost linear, it is extrapolated linearly to the time when the mixing was done.

This change of resistance, corresponding to the net change after mixing and the thermal compensation is denoted by ΔR_1, and the total electrical energy supplied by thermal compensation by Q_1, and the change of resistance after supplying a known amount of electrical energy Q_2 is denoted by ΔR_2, which is obtained by the similar procedure. The change of temperature is very small and the ΔR_1 and ΔR_2 is assumed to be proportional to the corresponding temperature change ΔT_1 and ΔT_2. Then the heat of mixing Q_m is given by

$$Q_m = Q_1 - \Delta R_1/\Delta R_2 \cdot Q_2$$

Typical plots of resistance versus time for the exothermic change, are shown in Fig. 8. In this case the change of resistance on mixing

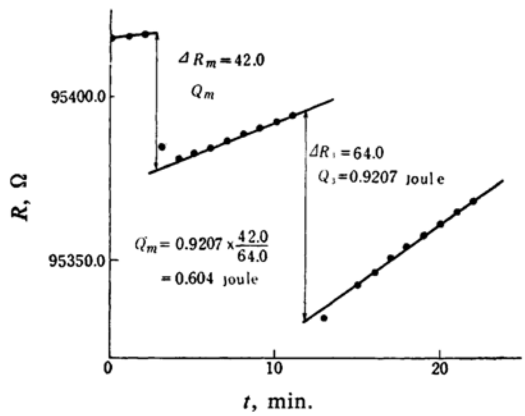

Fig. 8. Typical resistance vs. time curve for exothermic heat of mixing.

ΔR_m is obtained by linear extrapolation of the plots of resistance-versus time as described above. If the change of resistance due to the supply of a known amount of electrical energy Q_3 be ΔR_3, the heat of mixing for this case is given by,

$$Q_m = \Delta R_m/\Delta R_3 \cdot Q_3$$

by assuming again that ΔR_m and ΔR_3 are proportional to the corresponding change of temperature ΔT_m and ΔT_3.

The Sensitivity and the Errors. — The heat sensitivity is about 10^{-2} joule/Ω and the change of resistance can be measured precisely to 0.1 Ω, and thus the change of heat of 10^{-3} joule can be detected.

The errors in the final result may arise from the following sources;

1) the error due to the measurement of time,

2) that due to the measurement of the current which passes through the calorimeter heater,

3) that due to the weighing and the filling of the samples,

4) that due to the omission of the correction of heat exchange between the calorimeter and the surroundings.

For 1 the frequency of the crystal oscillator is precise to $\pm 10^{-5}$, and the error in counting is $\pm N$ count, where N is the number of operation of the gate circuit. N is usually within five, and one count corresponds to 10^{-4} sec. and the integral time registered on the counter is from 10 to 100 sec., the relative error in the measurement of time is between 5×10^{-5} and 5×10^{-6}.

Thus the total number of errors due to 1 is at most $\pm 5\times10^{-5}$.

For 2 the potential drop acrose the 10 Ω standard resistor is measured accurately to $\pm 0.5\times10^{-4}$ V. The current is of the order of a few to several tens of mA, then the potential drop across the standard 10 Ω resistor is of the order of several tenths of a volt. The relative error is at most $\pm 5\times10^{-4}$.

The resistance of the calorimeter heater is measured accurately to ±0.005 Ω in about 50 Ω. The relative error in the precision is $\pm 10^{-4}$.

For 3 the weighing of the samples is performed with the error of 0.5 mg. and the minimum weight of the samples taken is of the order of 100 mg. Then the relative errors would be at most $\pm 5\times10^{-3}$.

In the filling processes is sometimes occurs that a very small quantity of mercury enters into the needle of the syringe which can not be noticed until the next filling. When it is noticed, the drop of mercury is taken into a weighing bottle and is weighed and the correction is made to the former weight of the liquids.

If it is left unnoticed or noticed in the fillings after the next or further filling, then the correction cannot be made and this amounts to a few milligrams. In this case, the errors from this source may amount to a few per cent at most.

For 4 no quantitative evaluation can be made because during the course of thermal compensation the temperature versus time relation can not be recorded by this apparatus.

In a course of inspection of the data, it was noticed that when the compensation currents had been large, the values of heats absorbed obtained by the above mentioned procedure were a little greater than that when the compensating current had been small.

The errror due to the heat exchange in the endothermic cases might be a few per cent. In the exthermic cases the error due to linear extrapolation might be a few per cent, and in endothermic cases this kind of error may be extremely small due to thermal compensation.

The final error arising from all these sources above mentioned, though the errors from 3 and 4 are the largest, may amount to a few per cent.

Summary

A semi-automatic microcalorimeter is constructed which is convenient for a large number of the measurements of heats of mixing of two kinds of liquid.

The calorimeter is equipped with a removable mixing vessel, its holder, and a container, by which the efficiency of the measurement is much increased. Automatic registering of the time intervals during which the electrical current is supplied to the calorimeter, as well as automatic thermal compensation for endothermic systems, are performed. It is another feature of the apparatus to require only less than 1 cc. of each component for each measurement. The elimination of the vapor phase of the liquids in the mixing vessel makes the results certain. The heat sensitivity is 10^{-3} joule.

The author wishes to express his thanks to Professor R. Fujishiro of Osaka City University and to Professor Y. Morino of the University of Tokyo for their constant encouragement throughout this work.

Department of Chemistry
Faculty of Science
Kobe University
Higashinada-ku, Kobe