

COMMUNICATION (I)

A calorimetric technique of measuring low heat of solution

RINGKASAN

Satu kalorimeter yang mudah telah disusun khusus bagi menyukai haba larutan. Bahan utama bagi termostat ialah asid dekanolik. Perubahan suhu menghasilkan daya elektromotif pada termokupel tembaga-konstantan. Voltan kecil ini disukai dengan satu jangkavoltanmikro dan dibesarkan sebelum direkodkan.

SUMMARY

A simple calorimeter has been assembled specially for the measurement of low heats of solution. Decanoic acid was used as a thermostatic material. A change in temperature induces an emf in a copper constantan thermocouple. This small voltage is measured with a microvoltmeter, amplified and recorded.

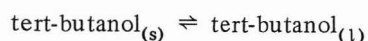
INTRODUCTION

The calorimeter to be described has been developed mainly for the purpose of measuring the heats of solution of various hydrated salts. A simple calorimeter which can be constructed from a Dewar flask, a stirrer and a Beckman thermometer cannot give good accuracy when the heat of solution of a given sample is very low. For example, nickel sulphate hexahydrate has a heat of solution of about 6 cal/g (Jamieson *et al.*, 1965). For a calorimeter of capacity 1 litre, the heat capacity is about 1×10^3 cal/°C. The temperature change due to the dissolution of a one-gram sample is therefore about 6×10^{-3} °C. The uncertainty of the Beckman thermometer is $\pm 2 \times 10^{-3}$ °C. Thus the error can be as high as 30%. The new calorimetric assembly is able to detect the heat change due to the dissolution of a sample to within ± 0.4 J which is about 2% of 6 cal. The error would obviously be even smaller if the heat of solution of the sample used were larger.

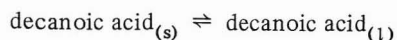
In a system that uses a thermocouple as a thermometer, temperature is recorded as induced *emf* that depends on the temperature difference between the hot and cold junctions. For example, if the temperature of the cold junction T_1 is 0°C, the melting point of ice, and the temperature of the hot junction is 25°C (room temperature in temperate countries) the *emf* developed is 0.990 mV for a copper-constantan pair. To measure

this, a voltmeter with one millivolt working range is adequate. However, the dissolution of a sample would usually cause a change of about 10 microvolts. This is only 1% of the working range.

The problem could be overcome if the initial *emf* induced by the temperature difference, $T_2 - T_1$, were very small so that a voltmeter with a more sensitive working range could be used. This requirement could be obtained by bringing T_1 as close as possible to T_2 . In a temperate climate, the equilibrium temperature for



at 25.5°C is excellent for T_1 . However in a tropical country, the equilibrium temperature for



at 31.5°C is suggested. With this arrangement, the *emf* induced is about 0.08 mV. This can be easily measured by a voltmeter with 100 microvolt working range. A temperature change that causes an *emf* change of about 10 microvolt would be significant and easily measured.

The assembly is schematically drawn in *Fig. 1*. A water-bath of dimension 30 × 30 × 20 cm (1) was filled with water and thermostated to 31.5°C. A plastic bucket (2) of 22 cm diameter was immersed in it. A small plastic bottle (3) which was

cut to accommodate the 300 ml Dewar flask (4) was glued to the centre of the base of the bucket. The bucket was then filled with decanoic acid and covered with a wooden cover. Two holes were made in the cover to accommodate two small glass tubes to contain the cold junctions of a pair of copper-constantan thermocouples arranged in series.

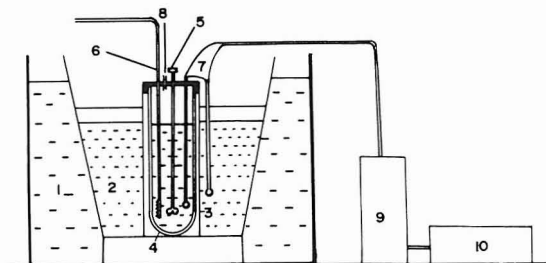


Fig. 1. Schematic diagram of the calorimetric assembly.

1. water bath 2. decanoic acid 3. plastic bottles
4. Dewar-flask 5. stirrer 6. heater 7. thermocouple leads 8. funnel 9. microvoltmeter 10. recorder.

The Dewar flask was fitted with a cover with holes to accommodate a mechanical stirrer (5) run at about 60 rpm, a 4.7-ohm heater of chromel

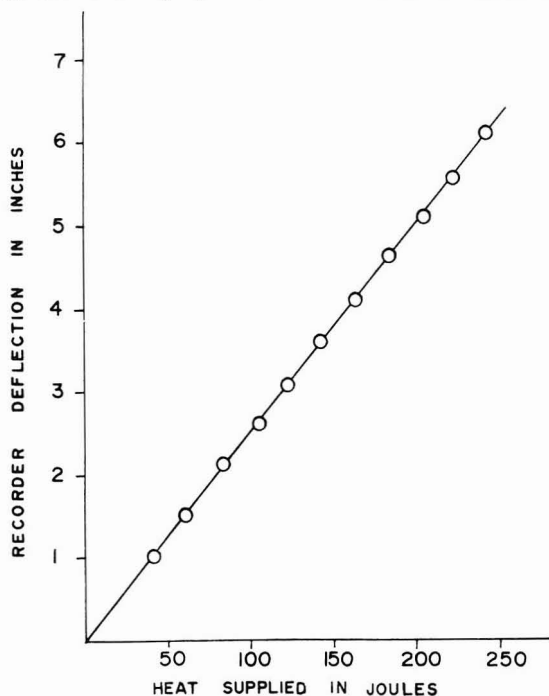


Fig. 2. Calibration of the calorimeter by measuring the recorder deflection caused by various energy inputs from a heater.

wire (6) the hot junction (7) and a small glass funnel (8) for sample delivery. The two ends of the thermocouples were connected to a DC Microvoltmeter, TOA Electronics Ltd, Model PM-16A (9). To facilitate recording, the outputs of the voltmeter were connected to a ten millivolt recorder (10).

The heat capacity of the calorimeter has been tested for its consistency by measuring the recorded deflections produced by various energy inputs. The results are plotted in Fig. 2. The slope is 39.6 ± 0.6 J/in. The linearity of the graph indicates the proportionality of the heat change and temperature rise to the deflection of the recorder pen within the working range.

The calorimeter has also been shown to give reproducible results. The heats of solution of six samples of $K_2SO_4 \cdot Co(H_2O)_6SO_4$ are given in Table 1. The mean value of 106 J/g with an error of ± 1 J is quite satisfactory for such a simple procedure.

Table 1
Heat of Solution of $K_2SO_4 \cdot Co(H_2O)_6SO_4$.

Sample weight (g)	Heat of solution (J/g)
0.1769	104.6
0.1448	104.4
0.2093	106.0
0.1750	103.5
0.2106	107.7
0.3631	106.8

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