A VACUUM ADIABATIC CALORIMETER FOR SPECIFIC HEAT STUDIES IN LIQUID MIXTURES, ESPECIALLY IN THEIR CRITICAL REGION

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ABSTRACT

The construction, operation and assessment of a vacuum adiabatic calorimeter, suitable for specific heat studies in liquid mixtures near their critical solution temperatures in the range 30—70° C, *are described. Examples of studies near the C S T of methanol-n heptane are given. Measurements on pure liquids give the* C_p *(in J/g deg) of* CH_3OH *as* $2{\cdot}08_1+1{\cdot}24_4\times10^{-3}\,t+3{\cdot}01_3\times10^{-5}\,t^2$ *in the temperature range* $35<t<60°C$, *of* CH_3CN *as* $2{\cdot}18_3+1{\cdot}80_0\times10^{-3}\,t+9{\cdot}20_0\times10^{-7}\,t^2$ *in the range* $45°<t<60°C$, *and of* CS_2 *as* $1{\cdot}02_4+5{\cdot}64_6\times10^{-4}\,t+4{\cdot}04_4\times10^{-7}\,t^2$ *in the range* $30<t<47°C$.

1. INTRODUCTION

There have been a number of interesting studies on the behaviour of equilibrium properties in the vicinity of the critical point in liquid-gas systems and magnetic systems. The behaviour of specific heat, in particular, is represented by an asymptotic divergence to infinity which is either logarithmic or of a weak power law form. Such a singularity in specific heat has aroused interest in studying the behaviour in binary liquid systems near their critical solutions temperature, since the phenomena exhibited by a binary mixture is closely connected with those in fluids and magnets.

With a view to study the behaviour of specific heat in the vicinity of the critical solution temparature in binary liquid mixtures, an adiabatic vacuum calorimeter, described in this paper, has been designed and built. Although the calorimeter has been developed greatly over the years[1], there

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are special features in work near the critical points. The main problem in studying the specific heat near critical points is the slow attainment of thermal equilibrium. Extended time scales involved in thermal measurements close to the critical point call for specific design of the calorimetric apparatus such that the accuracy is not lost due to the inevitable heat loss over the period of measurement. Also, the specific heat exhibits large variations close to the critical point and considerable resolution in temparature is required. to approach the critical point closely. These considerations on the measurements of heat capacity in the critical region of binary liquid systems, recommended the use of non-isothemal methods of calorimetry.

In a non-isothemal method, the heat capacity is determined in terms of the temparature change produced in the calorimeter and contents. If Q is the total heat supplied, C the heat capacity of the calorimeter and its contents and q the heat loss from the calorimeter to surroundings then C is given by $C=(Q-q)\frac{\Delta t}{\Delta T}$, where ΔT is the temparature rise produced in the time interval Δt. In view of the large time scales involved in the measurements near critical solution temparatures, the heat loss q between the calorimeter and its environments may become large and even be comparable to the total heat Q supplied. It is therefore necessary to minimize the heat loss as far as possible, by maintaining the ambient temparature close to that of the calorimeter. Under strict adiabatic conditions q is made zero. However, in practice, deviations from strict adiabaticity occur, and a small correction for heat leak has to be made[1].

2. CALORIMETRIC APPRATUS

Fig. 1 shows the general arrangement of the calorimetric appratus. The assembly essentially consists of the calorimetric vessel (sample holder), which is surrounded by the adiabatic shield. The latter is in turn surrounded by the floating shield, and the assembly is contained in a vacuum jacket, which also serves as a constant temparature environment for the inner parts. The vacuum jacket is mounted on a stand which could be raised or lowered smoothly, and is attached to the top flange by means of a neoprene 'O'-ring. The top flange is in turn connected to a high vacuum system. The teflon bolts (Fig. 1) used to suspend the floating shield and the adiabatic shield ensure complete rigidity of the assembly, in addition to providing thermal insulation. The calorimetric vessel is suspended by means of a fine silk fibre from the floating shield. All the electrical leads are thermally anchored to the bottom of the floating shield. This ensures that the various leads from the caloremetric vessel, adiabatic shield, etc., do not see the room temparature directly and are subjected to a much less temparature gradient. In this set up, access to the calorimeter could be gained by removing the bases of the floating shield and the adiabatic shield.

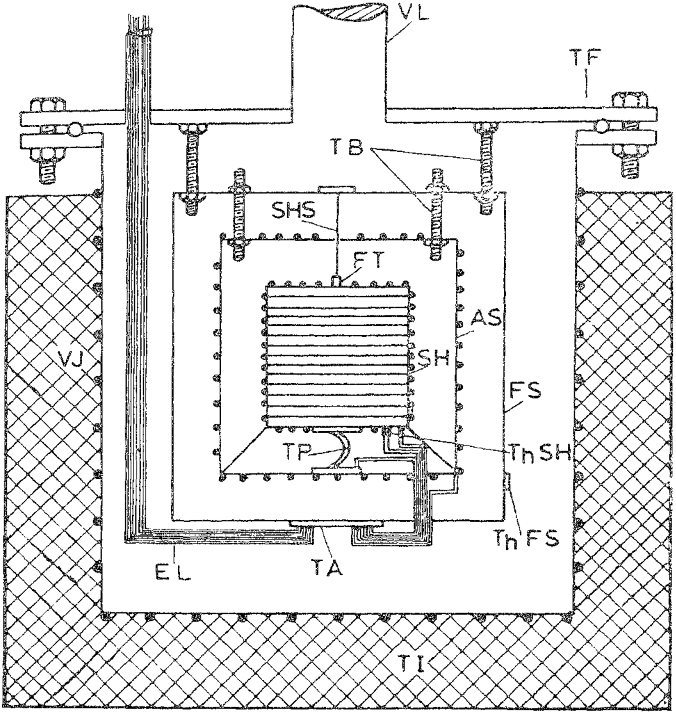

FIG. 1

Calorimetric apparatus (schematic). VL—vacuum line;
EL—electrical lead; SHS—sample holder suspension;
FT—filling tube; TF—top flange; TB—teflon bolt;
AS—adiabatic shield; VJ—vacuum jacket;
SH—sample holder; FS—floating shield; ThSH—thermometer on sample holder; ThFS—thermometer on floating shield; TP—thermopile; TA—thermal anchoring; TI—thermal insulation.

The general design considerations advocated by McCullough and Scott[1] have been incorporated in the appratus, but some special feature should be indicated briefly.

2a. CALORIMETRIC VESSEL

Both silver and copper have been used as materials for the sample container. It is a cylindrical vessel of about 60 c.c. capacity and about 0.6 mm. in thickness. To promote thermal equilibrium within the body of the liquid sample, a large number of thin fins have been welded to the body of the sample holder, so that each fin acts as an isothermal surface. Thus no part of the liquid in the calorimeter is away from an isothermal surface by more than about 1 mm. The filling tube and the sealing cap, both of stainless steel, are attached to the top lid. Power is supplied to the sample by winding a heater of 40 S.W.G. manganin wire, bifiliarly into fine grooves cut in the body of the calorimeter.

2b. ADIABATIC SHIELD

The adiabatic shield is cylindrical in shape and is of diameter 8 cms. and height 8 cms. It has been made out of copper-foil of thickness about 0.005″. Heater wire of 40 S.W.G. manganin has been wound on the body, top and the bottom of the shield. Adiabatic conditions surrounding the sample holder are achieved as follows: the vacuum 10^{-5} mm Hg renders the conduction and convection losses *via* the air medium negligible, and only the radiation loss is required to be eliminated. To do this, a 14 junction copper-constantan thermopile is connected between the sample holder and the adiabatic shield. The thermocouple junctions are attached to silver foils directly soldered to the calorimeter and the adiabatic shield. This procedure ensures high thermal response in detecting instantaneous temperature differentials. The thermopile output is directly fed on to a highly sensitive, quick response galvanometer. By manually adjusting the power to the adiabatic shield, the galvanometer deflection is maintained zero throughout an experiment.

2c. FLOATING SHIELD

The floating shield made of copper, is also cylindrical in shape, having a diameter of 11 cms. and height 11 cms. The uncontrolled floating shield serves three purposes: (i) it cuts out the radiant heat transfer between the outer jacket and the calorimeter by about 16%. (ii) it damps out any drastic temperature fluctuation in the environment affecting the calorimeter. (iii) it serves as a convenient place for thermally anchoring the electrical leads.

2d. VACUUM JACKET

This is a strong brass vessel of diameter 18 cms. and height 18 cms. to which is hard soldered a mild steel flange for O-ring seating. The vacuum jacket also serves the purpose of a thermostat, providing a constant temperature environment to guard the inner parts of the assembly. Heater of constantan material has been uniformly wound on the surface of the jacket. A thermister bead wrapped in a copper foil has been directly soldered on to its surface, to sense the temperature.

The sample temperature is known by measuring the resistance of a thermistor fixed on the surface of the calorimeter. The thermistor resistance could be represented over a small range of temperature by relation $R = ae^{b/T}$, where a and b are constants. The thermistor employed for temperature measurement has $R \sim 1{\cdot}5$ kiloohms. at 25°C, $b \sim 3310$°K and $a \sim 0{\cdot}207$ ohm. The thermistor has been repeatedly calibrated against the normal boiling points of several organic compounds by using Swietoslawski ebulliometer. With this method of calibration, differential temperatures are known correct to ± 3 millidegrees, and the absolute temperatures are determined to an accuracy of ± 50 millidegrees. The thermistor resistance is measured by means of an a.c. bridge network used in conjunction with a lock-in amplifier system which will be described in a separate communication. The bridge output is either observed on an oscilloscope or a d c. detector after phase detection. Changes in thermistor resistance $\sim 0{\cdot}1\Omega$ could be easily detected and this corresponds to a temperature resolution of 3 millidegrees.

The power to the sample heater is supplied by a well-stabilized 12V d.c. source. The power supplied to the sample is known by measuring the voltage across the sample heater end the current through it using standard resistances and a vernier potentiometer. The adiabatic shield is powered by a 0-30 V stabilized d.c. power supply. An on-off temperature control mechanism has been built to control the temperature of the vacuum jacket.

3. EXPERIMENTAL PROCEDURE

The calorimeter is filled in a 'dry box' and the filling tube sealed. The exact amount of the sample filled is determined by weight. The calorimetric assembly is evacuated to a high vacuum of about 10^{-6} torr and the apparatus is degassed for about 30 hours before starting the measurement.

In operating the calorimetric apparatus, the continuous heating method is employed. This method essentially consists in continuously supplying power to the calorimeter and measuring the rate of rise of temperature.

Heating rates between 0.5°C per hour and 10°C per hour are chosen. The power to the adiabatic shield is also continuously adjusted to maintain its temperature to within 5 millidegrees of that the calorimeter at every instant. The a.c. thermistor bridge is balanced and simultaneously a stop watch is started. The balancing resistance in the bridge is continuously set at a slightly lower value (corresponding to a given temperature increment of the sample) and the time interval between successive balance positions in the bridge is recorded. Thus by reducing the bridge resistance in small steps and timing the intervals continuously, the time-temperature history of the sample can be obtained. One other fact is worthy of mention. At any equilibrium state the jacket temperature is maintained close to that of the calorimeter to within 10 millidegrees, thus guarding the inner parts of the assembly from ambient temperature fluctuations. With low thermal inertia of the jacket, its temperature can be programmed to follow that of the calorimeter at every instant. This procedure renders the adiabatic shield control easier, because quite low power is adequate for control.

4 THE PERFORMANCE OF THE CALORIMETRIC APPARATUS

The performance of the apparatus has been studied by making heat capacity measurements with the sample holder empty (empty run) and with the sample holder filled with two standard substances, water and *n*-heptane.

Empty Run:

The sample holder has been sealed with air at atmospheric presure. The temperature range 40°–60°C has been found adequate for studies on binary liquid systems. The heat capacity of the sample holder is found to be about 30J/deg in the temperature range covered. The consistency in the data between different heating rates ensures that the heat losses involved are less than 1%. Assuming that the thermal anchoring of the lead-in-wires is good and that the pressure is about 10^{-5} torr, a detailed estimate of the magnitude of the heat transfer between the calorimeter and its surroundings gives the following values: Conduction loss *via* the electrical leads from the calorimeter to the floating shield is $\sim 5\times 10^{-4}$ J/sec.; radiation loss between the calorimeter and the adiabatic shield (for maximum of 10 m. deg. temperature differential) is $\sim 10^{-4}$ J/sec; conduction loss through air at the prevailing vacuum is $\sim 5\times 10^{-6}$ J/sec. The heat losses through the teflon bolt suspensions are all even less. Typically, the energy supplied at the lowest heating rate to the sample is $\sim 8\times 10^{-2}$ J/sec. The sum total of the losses is thus seen to be just about 1%. However, the accuracy of the calorimeter apparatus has been unambiguously determined by making measurements on standard calorimetric substances such as water and heptane.

5. WATER AND HEPTANE RUNS

Two different runs have been made with the calorimeter half-filled and almost filled with water. The temperature variation of the specific heat of water has been studied at the NBS by Osborne *et al*[2]. The present data agrees to within 1% with the NBS values in the temperature range 45 – 60°C. Also, from the measured heat capacity of water in the two runs, the contribution to the total heat capacity by empty calorimeter can be deduced This value of the empty calorimeter heat capacity agrees with the experimentally determined value to within 1%, indicating that heat losses in the covered temperature range are within 1%.

n-heptane has been chosen as a calorimetric substandard and its specific heat has been very accurately measured in the NBS by Douglas *et al*[3]. Measurements have been made with *n*-heptane and the present data on its specific heat in the temperature range 35 – 60°C agree within 1% of the NBS data. Thus the measurements with water and heptane indicate that the absolute accuracy obtainable with the present calorimetric apparatus is about 1%.

6. RESULTS OF THE SPECIFIC HEATS OF METHANOL, ACETONITRILE AND CARBONDISULFIDE

The calorimeter has been used to determine the specific heats of CH_3OH, CH_3CN and CS_2 While a silver calorimeter was used for measurements on CH_3OH, a copper sample container was used for CH_3CN and CS_2. Fig. 2 depicts the observed temperature variation of the specific heat of CH_3OH, determined with three different heating rates. A smooth curve has been drawn through the experimental data and a comparsion is made of the present data with those of the earlier workers 4, 5, 6 as shown in the figure. The variation of the specific heat of CH_3OH is found to be about 8% in the temperature range 35 – 60°C.

The specific heat of CH_3CN also shows a normal increase of about 2%, in the temperature range 45 – 60°C, as shown in Fig. 3 (a) Putnam *et al*[7] have made measurements of C_p on CH_3CN, but only upto 300°K and their curve when extrapolated smoothly passes through the present data points. For both CH_3OH and CH_3CN, no detailed measurements above room temperature have been made earlier.

Fig. 3 (b) shows the specific heat data of CS_2, and since CS_2 is sealed in the sample container with air at atmospheric pressure it can not boil at any temperature under these conditions. In the entire temperature range covered in the experiment C_p shows about 2% rise. Also the present C_p values are in good agreement with the C_p values reported by Staveley *et al*[8].

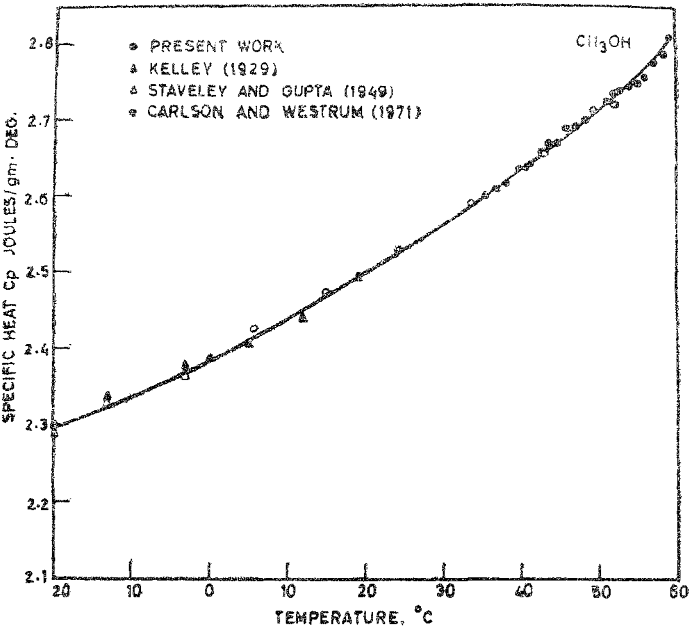

FIG. 2

Comparison of the present specific heat data of methanol with the earlier data.

The specific heat variation of these three liquids can be represented by a relation of the form :

$$C_p = A + Bt + Ct^2 \text{ ; } (t \text{ in } ^\circ\text{C})$$

The present data have been fitted to the above relation, and the values of the co-efficients A, B and C are given below

Compound	Temp. range	A	B	C
		J/gm (deg	J/gm (deg)^2	J/gm (deg)^3
CH_3OH	35 – 60°C	$2{\cdot}38_1$	$1{\cdot}24_4 \times 10^{-3}$	$3{\cdot}01_3 \times 10^{-5}$
CH_3CN	45 – 60°C	$2{\cdot}18_3$	$1{\cdot}80_0 \times 10^{-3}$	$9{\cdot}20_0 \times 10^{-7}$
CS_2	30 – 47°C	$1{\cdot}02_4$	$5{\cdot}64_6 \times 10^{-4}$	$4{\cdot}04_4 \times 10^{-7}$

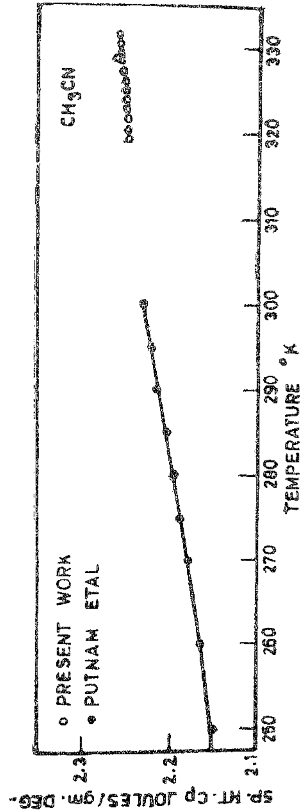

Fig. 3 (*a*)

Comparison of the present specific heat values of acetonitrile with the earlier data.

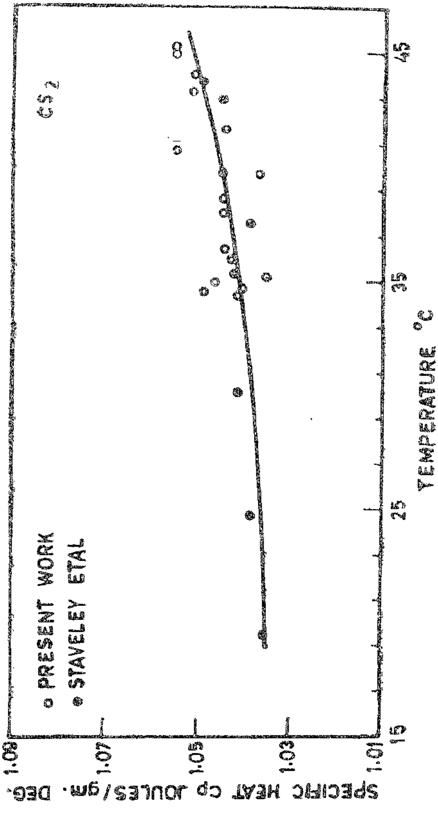

FIG. 3 (*b*)

Comparison of the present specific heat values of carbon-disulphide with the earlier data.

7 SPECIFIC HEAT MEASUREMENTS NEAR THE CRITICAL POINTS OF BINARY LIQUID SYSTEMS

The same adiabatic calorimeter has been used to study the specific heats of a number of binary liquid mixtures over the entire composition range and temperature interval 40–60°C, with special emphasis on the critical solution region. Particular attention has been paid to the slow attainment of thermal equilibrium of the liquid samples in the region close to the critical temperature T_c. Measurements have been made at heating rates as low as 1°C/hr so that the measured values correspond to the true equilibrium state of the system. It can be rementioned in the present context that the performance of the calorimeteric apparatus at such low heating rates has been checked with standard substances. In the vicinity of T_c the calorimetric stepwidth has been reduced so that, the transition could be approached with a resolution of $|T-T_c| \sim 30$ millidegrees, corresponding to $|(T-T_c)/T_c| \sim 9 \times 10^{-5}$ ($T_c \sim 320°K$). Fig. 4 shows the specific heat anomalies observed in the critical region of the binary liquid system methanol-n heptane, with $X_c = 61.35$ mole % methanol and $T_c = 51.87°C$. As seen from the figure the anomaly is well pronounced in a narrow range around (X_c, T_c). With higher resolution [$|(T-T_c)/T_c| < 10^{-4}$], the specific heat values are accurate to only about 10% due to large random scatter. The same fact has been expressed by Voronel and Coworkers[9] who point out that the smallest temperature interval over which they have been able to measure the specific heat with reasonable accuracy is 40-50 millidegrees. Obviously one should have higher precision in the control and measurement of temperature to approach T_c closer than 10^{-4} in $|(T-T_c)/T_c|$.

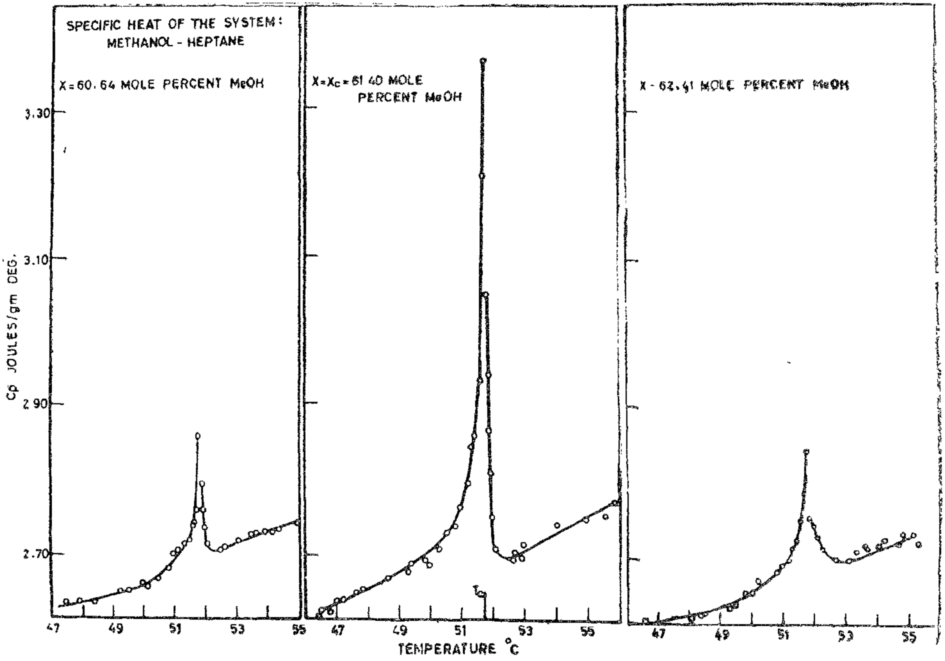

FIG. 4

Specific heat anomalies in the critical region of the binary mixture methanol—n. heptane.

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