

VAPOUR PRESSURE, HEAT OF EVAPORATION AND THERMAL CONDUCTIVITY DETERMINATION  
BY MEANS OF THE C 80 CALORIMETER

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SUMMARY

Calorimeters are among the most valuable tools for thermodynamic investigation. Their application field is expanding by the development of new experimental set-ups, designed to measure :

- vapour pressure and heats of evaporation of liquids ;
- thermal conductivity of liquids and gases.

INTRODUCTION

The C 80 calorimeter is used to investigate melting, transitions, reactions, decomposition, solubility, heat capacity in a wide range of temperature (ambient to 573 K) and pressure (from a few Pa to 30 MPa) (1). Both temperature and pressure can be controlled. The pressure during a process such as decomposition can either be preset or monitored while the heat generated is measured. All these information are most valuable and are required by the petroleum industry. The application field of the C 80 calorimeter is expanding, as new experimental set-ups are designed to measure vapour pressure, heats of evaporation of liquids and thermal conductivity of liquids and gases.

HEAT OF EVAPORATION OF LIQUIDS

A special vessel which fits inside the C 80 calorimeter is filled with the liquid. The temperature of the calorimeter is preset at a value between ambient and 200°C. The liquid is evaporated by drawing vacuum. The signal from the calorimeter provides after integration the heat of evaporation with a reproducibility of 1 % and an accuracy better than 3 %. After testing this technique with toluene, water and benzene, the heat of evaporation of types petrol is measured. (Table 1).

TABLE 1

The following values of heat of evaporation were measured.

	Measured values (J/g) $\Delta H_{exp}$	Literature values (J/g) $\Delta H_{th}$	$\Delta H_{exp} - \Delta H_{th}$ $\Delta H_{th}$ (%)
Toluene	397 at 308.5 K	406 at 308.5 K	2.1
Water	2 376 at 308.5 K	2 418 at 308.5 K	1.7
Benzene	414 at 308.5 K	426 at 308.5 K	2.7
Petrol unleaded	339 at 318.6 K		
Diesel oil	362 at 318.6 K		

#### VAPOUR PRESSURE OF LIQUIDS

This is measured by applying an opposing pressure of helium while monitoring the signal from the calorimeter (Figure 1). The value of the vapour pressure is equal to that of the opposing pressure stopping the evaporation, this being followed through the power signal provided by the calorimeter. The reproducibility of the measurement is in the order of 0.5 % and the accuracy 1 %.

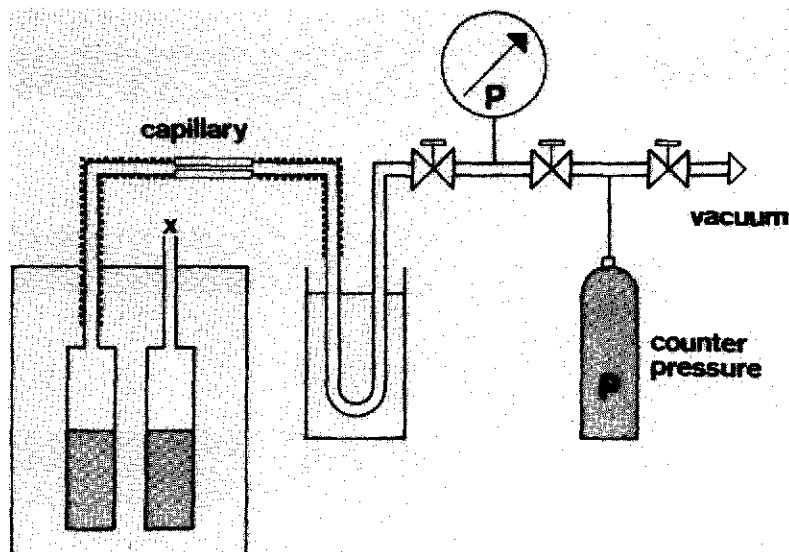
By following this procedure, the vapour pressure of toluene was measured at 393.8 K (120.8°C) (Figure 2) and its value is 0.135 MPa (1.33 bars), which is in very good agreement with the value (1.326 bar) found in the literature. (Figure 1)

#### THERMAL CONDUCTIVITY OF LIQUID AND GASES

The thermal conductivity characterizes the ability of a material to transfer heat. Its values cannot always be found in the appropriate literature. It can now easily be measured by means of a new set-up which fits inside the C 80 calorimeter. (Figure 3)

The set-up is designed on the coaxial cylinders principle. The fluid, the conductivity of which is measured, is located between the two cylinders : a container and an insert. The latter is made of copper which has a high heat conductivity. The former in stainless steel fits in the space surrounded by the heat flux transducer.

Inside the wall of the container, there is a heating coil in which constant power is generated by Joule effect. It will flow from the heating coil into the heat sink of the calorimeter through two ways. A first part will flow through the heat flux transducer and the other one through the fluid into the insert which forces it into the heat sink. The former is monitored by the calorimeter. At a given temperature for a fluid with a thermal conductivity of  $\lambda$ , the measured signal  $S$  and  $\lambda$  are linked by :



### C.80 calorimeter

Fig. 1. Experimental set-up to measure vapour pressure of liquids by means of the C 80 calorimeter.

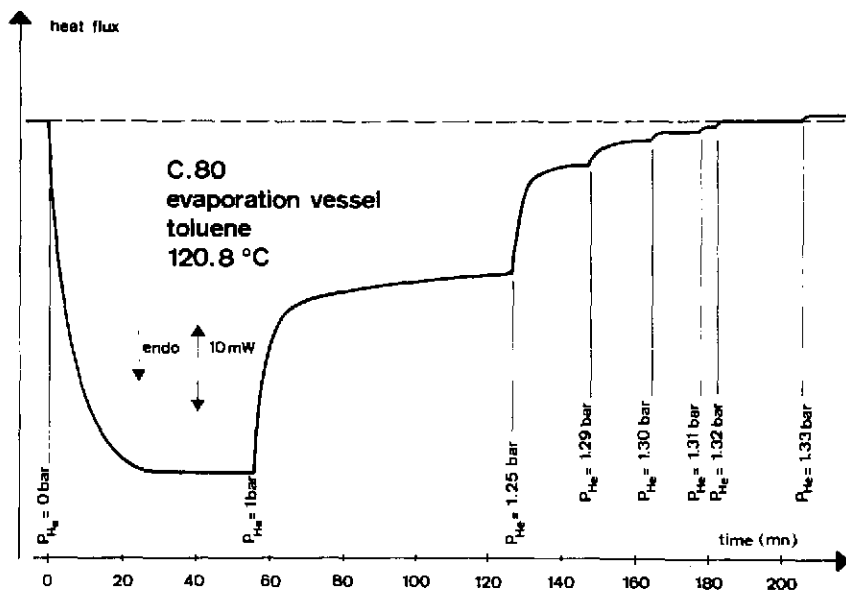


FIG. 2. Vapour pressure determination of toluene at 393.8 K (120.8°C)

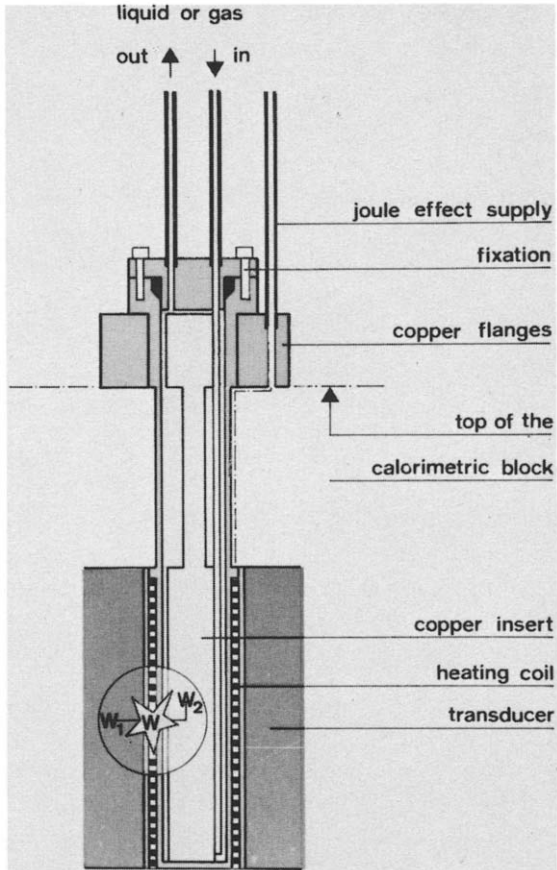


Fig. 3. Experimental set-up to measure heat conductivity by means of the C 80 calorimeter.

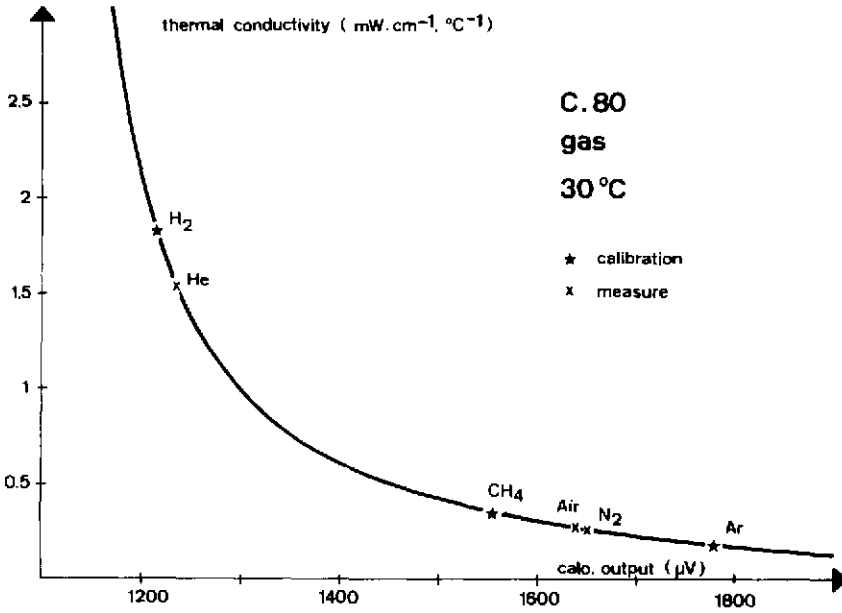


Fig. 4. Thermal conductivity determination of gases.

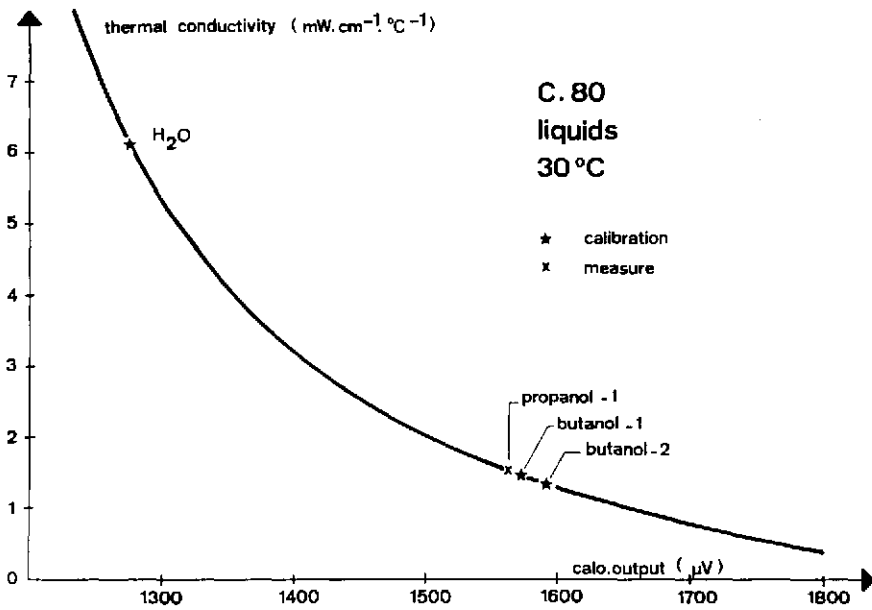


Fig. 5. Thermal conductivity determination of liquids.

$$\lambda = \frac{-S + A}{BS + C}$$

where A, B, C are constant values, which can be determined by using 3 standards such as hydrogen, methane and argon.

The thermal conductivity coefficient is then plotted as a function of S and the values of helium, air and nitrogen are calculated with a reproducibility better than 1 % and an accuracy of 1 % (Figure 4).

Good resolution by this method enables the thermal conductivity coefficients of air and nitrogen to be differentiated. These are very close.

For liquids, water, butanol 1 and butanol 2 are all three chosen as standards for the determination of the curve which is then used to measure the thermal conductivity of propanol 1. (Figure 5)

#### CONCLUSION

New set-ups have been designed by SETARAM to measure heat of evaporation, vapour pressure of liquids and thermal conductivity of both liquids and gases. Their importance is such that combining the set-up with the C 80 calorimeter produces an instrument in itself.

#### REFERENCES

- 1 SETARAM application booklet (File 6) C 80 application.
- 2 Reddick and Bunge, Organic Solvents.