

HEATS OF SOLUTION FROM VAPOUR-LIQUID PARTITION CHROMATOGRAPHY*

By B. H. PYKE† and E. S. SWINBOURNE‡

The separation of benzene, *cyclohexane*, and *cyclohexene* by means of vapour-liquid partition chromatography was reported by Anderson and Napier (1956), who used a polyethylene-glycol-octyl-cresyl ether (PGCE) as a stationary phase. The heats of solution of benzene and *cyclohexane* vapour in PGCE liquid were also determined with this technique (Anderson and Napier 1957).

In a similar study we recently estimated the heats of solution of benzene, *cyclohexene*, *cyclohexane*, and *cyclopentene* vapours in PGCE, the values together with those of Anderson and Napier are presented in Table 1. Taking into consideration possible variation in technique and in quality of the stationary phase§

TABLE 1
HEATS OF SOLUTION OF HYDROCARBON VAPOURS IN PGCE LIQUID

Hydrocarbon Vapour	Heat of Solution (ΔH)		Latent Heat of Condensation (ΔH) (kcal/mole)
	Anderson and Napier (kcal/mole)	Pyke and Swinbourne (kcal/mole)	
Benzene ..	-7.5	-7.2	-7.5*
<i>cyclo</i> Hexene ..	Not determined	-7.0	-7.3*
<i>cyclo</i> Hexane ..	-5.3	-5.5	-7.2*
<i>cyclo</i> Pentene ..	Not determined	-5.1	-6.7†

* Values from Lange (1956).

† Estimated from Trouton's constants of like compounds, using the values obtained for the other compounds from Lange (1956).

there is good agreement in the case of the two substances studied commonly. Further, it is interesting to note that the heats of solution of benzene and *cyclohexene* are very close in magnitude to the corresponding values for the latent heat of condensation (also shown in Table 1). This comparison indicates that there is no great departure from ideal solution behaviour in these compounds

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† Ampol Petroleum Ltd., Balmain, N.S.W.

‡ School of Chemistry, University of New South Wales, Broadway, Sydney.

§ PGCE is used as a commercial detergent.

(see, however, discussion by Anderson and Napier 1956, p. 543). On the other hand, it appears likely that *cyclohexane* and *cyclopentene* are exhibiting *positive* deviation from the ideal vapour pressure/composition law; this would account for *cyclohexane* appearing in the eluate well in advance of benzene in spite of the higher boiling point of the former (benzene, b.p. $80.1^{\circ}\text{C}/760\text{ mm}$; *cyclohexane*, b.p. $81.4^{\circ}\text{C}/760\text{ mm}$).

The apparatus used in the present study was based upon that described by Ray (1954). Alumina-free refractory brick,* carefully ground and screened to -50 to $+100$ B.S.S. mesh, was used as a support for the stationary phase,

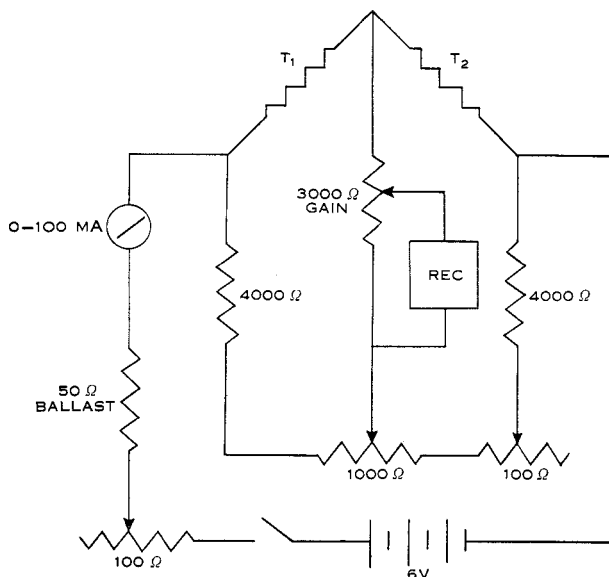


Fig. 1.—The detector circuit.

T_1, T_2 , thermistors (resistance $2000\ \Omega$ at 20°C); *Rec*, Leeds and Northrup Speedomax recorder ($0-5\text{ mV}$).

the carrier gas being dry nitrogen. Chromatographic runs were made at temperatures of 62.5 , 80 , and 100°C . The thermal conductivity cell was operated at room temperature, thermistors being used as the sensitive elements. Full details of the detector circuit are shown in Figure 1. (Forss and Stark (1958) have recently described similar circuits incorporating the same type of thermistor.) A more comprehensive discussion of the use of thermistors in thermal conductivity gas analysers has been given by Walker and Westenberg (1957).

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* Bricks of the "Morgan M.I. 23 and 28" type were originally used but owing to their high-alumina content were found to be unsatisfactory. Subsequently, the material used was a crushed "Diatom" brick manufactured by Messrs. Newbold General Refractories Ltd.

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