

## 5. *The Chromatography of Gases and Vapours. Part VI.\* Use of the Stearates of Bivalent Manganese, Cobalt, Nickel, Copper, and Zinc as Column Liquids in Gas Chromatography.*

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A series of retention times have been measured by use of gas-liquid chromatographic columns, in which the column liquids are molten stearates of manganese, cobalt, nickel, copper, or zinc. The behaviour of these columns towards different classes of vapour is compared with that of a more conventional column in which liquid Apiezon grease L is used. Particularly strong interactions have been found between amines and the metal salts.

THE use of metal salts in gas-liquid chromatographic columns is of interest as a possible means of obtaining selective separations as a result of interaction between vapours and the metal atoms. This was first demonstrated by Bradford, Harvey, and Chalkley<sup>1</sup> who used a solution of silver nitrate in ethylene glycol to achieve selective retardation of unsaturated hydrocarbons. We have used metal stearates at 156°, a temperature at which they are all liquid, but such systems may also serve as a model for the behaviour of purely inorganic salts which will probably be the most suitable liquid phases at column temperatures above 500°. The results obtained with the metal stearate columns may also be of interest as illustrating a method which may be useful for studying complex formation. For this reason we have chosen a group of metals whose aqueous complex-ion chemistry has been much studied.

### EXPERIMENTAL

The column material was packed into a glass tube of 4 mm. in diam., 100 cm. long. The column temperature was controlled by a vapour jacket. Nitrogen-hydrogen (1 : 3 v/v), used as carrier gas, was preheated before entering the column. The sample was introduced to the column by Scott's capillary method.<sup>2</sup> The chromatograms were recorded with a hydrogen-flame detector,<sup>2</sup> the output being fed from the thermocouple to a milliammeter recorder *via* a D.C. microvoltmeter (Pye, Cambridge). Gas flow-rate was measured on a soap-bubble flowmeter, corrections being made for the water vapour pressure of the soap solution.

Metal stearates, prepared by double decomposition, were supplied by the Watford Chemical Company, and contained up to 2% of sodium chloride. The cobalt salt was hydrated. The water was removed either by heating alone or in benzene solution. All values quoted in this paper are for the anhydrous salt. A sample of ferrous stearate was prepared but as this rapidly oxidised in contact with even small traces of air, it was not thought to be satisfactory as a column liquid. The manganese stearate was found to oxidise when heated in air at 160°. No stearate had a sharp m. p., but they softened gradually over about 5°. Clear liquids were obtained at the following temperatures: Mn 104°, Co 92°, Ni 146°, Cu 101°, Zn 122°. Apiezon L high-vacuum grease was supplied by W. Edwards and Co.

The stearate column liquids (19 parts) or Apiezon L (25 parts) were mixed with Celite (100 parts), a solvent which was evaporated off with continuous stirring being used. Suitable solvents were ether for Apiezon L, and benzene for all stearates except that of nickel, for which *cyclohexylamine* was suitable although it took many hours to remove.

The results given are derived from a large number of individual experiments. In order to check the stability of the columns and their reproducibility when packed in different ways and by different experimenters it was necessary to follow many separate runs, each containing one compound plus the internal standard (mesitylene) to avoid errors arising from competition for sites round the metal atoms. Thus Fig. 1 represents some 70 runs on the stearate and 50 on the Apiezon, similar work being done for the other stearates; for zinc stearate the experiments were repeated in a metal tube. The copper stearate column had to be

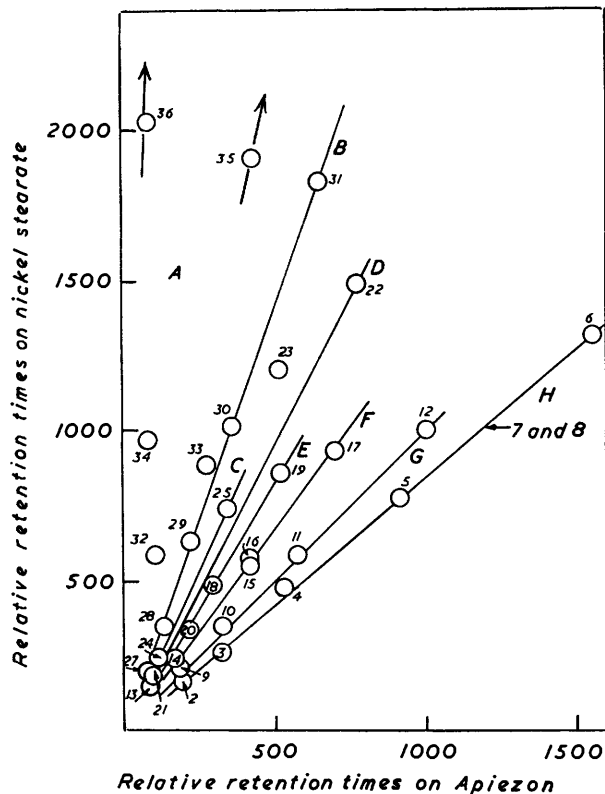
\* Part V, *J.*, 1955, 1480.

<sup>1</sup> Bradford, Harvey, and Chalkley, *J. Inst. Petrol.*, 1955, **41**, 80.

<sup>2</sup> Scott, "Vapour Phase Chromatography," ed Desty, Butterworths, London, 1957, p. 131.

remade frequently owing to its decomposition by certain vapours. Each point in Fig. 2 represents some 20 experiments. In addition, for each amine it was necessary (on one metal stearate column) to make a number of experiments to correct for the asymmetry of the peaks.

FIG. 1. *Relative retention times on nickel stearate and on Apiezon at 156°.*



1 Hexane, 2 heptane, 3 octane, 4 nonane, 5 decane, 6 undecane, 7 dodecane, 8 tetradecane, 9 benzene, 10 toluene, 11 *m*-xylene, 12 mesitylene, 13 ethyl methyl ketone, 14 diethyl ketone, 15 butyl ethyl ketone, 16 methyl pentyl ketone, 17 hexyl methyl ketone, 18 *cyclopentanone*, 19 *cyclohexanone*, 20 1 : 1'-dimethylbutanol, 21 1-methylpropanol, 22 1-methylheptanol, 23 *cyclohexanol*, 24 2-methylpropanol, 25 2-methylpentanol, 26 2-methylheptanol, 27 propanol, 28 butanol, 29 pentanol, 30 hexanol, 31 heptanol, 32 diethylamine, 33 dipropylamine, 34 *tert.*-butylamine, 35 aniline, 36 pyridine.

A, Amines; B, normal primary alcohols; C, 2-methyl alcohols; D, secondary alcohols; E, cyclic ketones; F, aliphatic ketones; G, aromatic hydrocarbons; H, aliphatic hydrocarbons; I, tertiary alcohols.

The point for 36 is 8073, 296; for 35 is 3811, 855; for 7 is 2205, 2670; and for 8 is 6290, 7775. The last two lie on line H, the first two in the direction of the arrows.

### RESULTS

Relative retention times at 156° were measured with mesitylene as internal standard (retention time taken as 1000). From these, plots were made as in Fig. 1 of relative retention times on metal stearate against relative retention times on Apiezon L. Each homologous series gives a good straight line passing through the origin, indicating that for each series there is a constant difference of free energy of solution between metal stearate and the Apiezon. The gradients of the lines measure the retardations (relative to mesitylene) of substances when passed through a metal stearate instead of Apiezon. They may thus be called retardation factors. Similar plots were obtained for all the metals, so that it is only necessary to report the retardation factors for the various homologous series, as

in Fig. 2. There is a maximum at nickel stearate and a minimum at copper stearate for all the series plotted. Such a pattern is strongly reminiscent of that obtained for complex stabilities for substitution at the fifth and sixth positions as found in studies of the metal ions in aqueous solution, where the effect has been interpreted in terms of ligand-field theory.<sup>3</sup> In each homologous series, as with other column liquids, the logarithms of the retention times give straight lines when plotted against the number of carbon atoms.

Very much stronger retardations are found when amines are passed through the metal-salt columns. Table 1 gives a set of relative retention times for manganese stearate where the effect is relatively small.

Fig. 2. Retardation factors for different metal stearates at 156° (curves lettered as for Fig. 1).

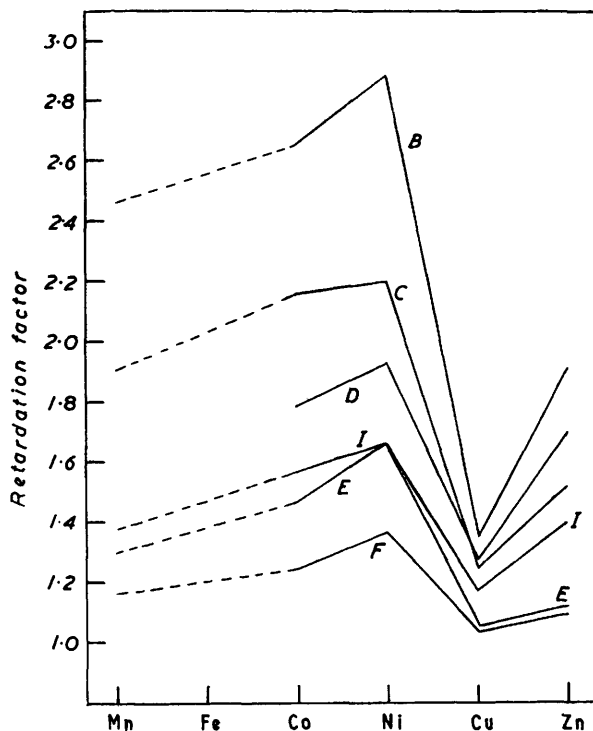


TABLE 1. Relative retention times for amines on Apiezon L and on manganese stearate columns at 156°.

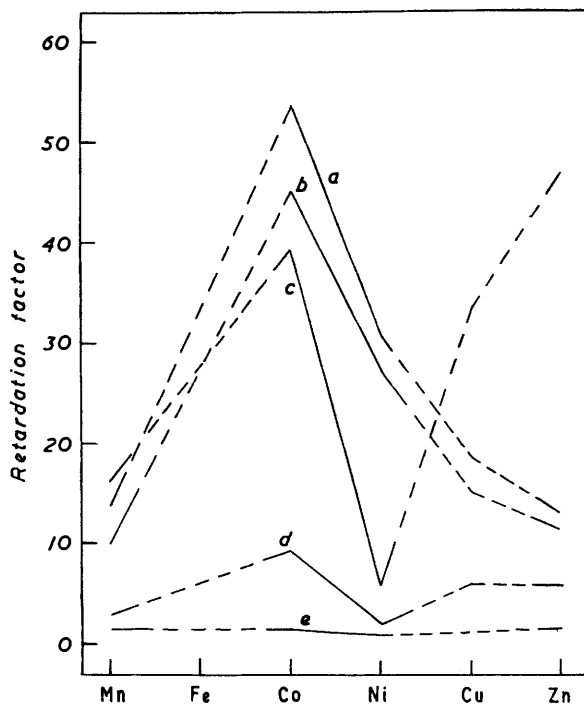
	Apiezon Stearate		Apiezon Stearate		Apiezon Stearate	
	Primary		Secondary		Tertiary	
Pr <sup>i</sup> .....	66	2304	Et <sub>2</sub> .....	99 1610	Et <sub>3</sub> .....	187 328
Pr <sup>n</sup> .....	173	3655	Pr <sup>n</sup> <sub>2</sub> .....	276 2134	Pr <sup>n</sup> <sub>3</sub> .....	619 649
Bu <sup>n</sup> .....	215	6032	Bu <sup>n</sup> <sub>2</sub> .....	758 4871	Bu <sup>n</sup> <sub>3</sub> .....	2382 3342
Bu <sup>t</sup> .....	79	1550				
			Aromatic amines			
Aniline .....	855	2084	α-Picoline	416 1230	2:6-Lutidine	571 661
N,N-Dimethylaniline	1835	1989	β-Picoline	535 7460	Pyrrole .....	202 301
Pyridine .....	296	3016	γ-Picoline	540 9670		

It has not yet been possible to obtain satisfactory results with primary amines for all the metal salt columns, but the general trends observed for the less strongly complexed amines are shown in Fig. 3. Accurate relative retention times for amines are difficult to

<sup>3</sup> Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 387.

measure because of the markedly asymmetric peaks (sharp fronts and diffuse tails) which result when any but very small samples are used. Thus, with pyridine, symmetrical peaks only occur with samples less than  $0.1 \mu\text{l}$ . The values quoted have been obtained either by using samples small enough to give symmetrical peaks, or by measuring from the back of the peak (the position of which remains constant with change of sample size) a distance equal to half the peak width for a non-complexed substance with a similar retention time. The latter method is naturally subject to an error which may amount to 2–3%, but in the cases where results have been obtained by both methods they agree very well. The sharp fronts and diffuse tails are presumably associated with competition among the amine molecules for sites, or the more favoured sites around the metal atoms.

FIG. 3. Retardation factors for different metal stearates at  $156^\circ$ .



*a*,  $\beta$ -Picoline; *b*, pyridine; *c*, diethylamine; *d*,  $\alpha$ -picoline; *e*, tributylamine.

With copper stearate both the shapes and relative retention times of amine peaks have been found to vary curiously with flow-rate. This is particularly so at flow rates greater than 20 c.c./min., and may be connected with some slow complexing process. The results plotted for copper stearate in Fig. 3 are for low flow-rates and for the normal sharp-fronted type of amine peak, but they have been marked by a broken line to indicate that there is some uncertainty attached to them. Primary amines decomposed the copper stearate column.

Retardation factors for secondary and tertiary amines with Mn, Co, and Zn stearates were proportional to the basic dissociation constants of the amines. This relationship did not apply to primary amines or pyridine homologues, where the retardation factors are relatively much greater (except for  $\alpha$ -substituted pyridines). For the primary amines there may perhaps be some effect involving hydrogen bonding of the amine to the stearate groups around the metal atom. For pyridine and  $\beta$ - and  $\gamma$ -picoline there is presumably some  $\pi$ -bonding from the metal which is absent from bonding to a proton.  $\alpha$ -Picoline

and 2 : 6-lutidine are very little retarded by the metal stearates, which suggests that there is steric interference from the methyl groups adjacent to the pyridine-nitrogen atom.

The results for the series diethylamine, dipropylamine, and dibutylamine are peculiar in that while the change is regular (by a factor of 2·8) along the series on Apiezon, this is not so on the metal salts. There is a somewhat similar phenomenon in tertiary amines.

The changes for the amines along the series of metals are difficult to understand in terms of simple complex-ion theory. The marked drop from cobalt to nickel stearate which is the particularly strange feature of the series may perhaps be correlated with some peculiarity of structure in nickel stearate, whose m. p. is greater than those of the other members of the series. A few results obtained with nickel oleate as column liquid suggest that here complexing and retardation of amines may be stronger than with cobalt stearate. Nickel oleate liquefies between 25° and 30°.

The special interactions with metal stearates make it possible to use these column liquids to effect separations which may otherwise be difficult. A suitable column for a specific separation at 156° can be deduced from the results in Figs. 1, 2, and 3 and Table 1, but for illustration we quote in Table 2 a few instances of pairs of substances which happen to be difficult to separate on Apiezon but can be quite easily separated on manganese stearate. Also given in Table 2 are the number of theoretical plates required for 99·9% separation, as estimated from the graph published by Glueckauf.<sup>4</sup> These values will only apply when sufficiently small samples are used to give symmetrical peaks for the amines.

TABLE 2. *Relative retention times (t) and numbers of theoretical plates (n) for separations on Apiezon and on manganese stearate columns.*

Compound	B. p.	t, Apiezon	n, Apiezon	t, Mn Ste.	n, Mn Ste.
$\beta$ -Picoline .....	143°	535	400,000	7460	600
$\gamma$ -Picoline .....	143	540	—	9670	—
$\gamma$ -Picoline .....	143	540	15,000	9670	5
2 : 6-Lutidine .....	143	571	—	773	—
n-Butyl alcohol .....	118	123	4000	356	250
isoButyl alcohol .....	108	111	—	244	—

The marked selectivity of metal stearates for certain specific groups might also be used to identify the class to which a compound belongs.

Relative retention times at 156° were reproducible during up to two months of column use. Some experiments with zinc stearate packed into a brass tube showed that the same relative retention times were obtained as in a glass tube. The metal stearate columns as used had theoretical plate numbers approximately 60% of those found for the Apiezon column.

*Thermodynamic Data.*—Specific retention volumes,<sup>5</sup>  $V_g$  (previously called corrected retention volumes per gram<sup>6</sup>), were obtained for mesitylene, the internal standard, at 156° and at 110·6°, by Littlewood, Phillips, and Price's procedure.<sup>6</sup> The values were  $V_g(156^\circ)$  68·1,  $V_g(110\cdot6^\circ)$  241·4. The density of cobalt stearate ( $\rho$ ) at 156° was 0·902 g./c.c. A series of relative retention times were measured on cobalt stearate at 110·6°. From these results free energies, heats, and entropies of solution were calculated by use of the relations

$$-\Delta G = RT \ln \alpha$$

$$\alpha = \frac{\text{Weight of vapour per unit volume of column liquid}}{\text{Weight of vapour per unit volume of gas}}$$

$$V_g = 273\alpha/T\rho$$

$$d \ln V_g/dT = \Delta H/RT^2$$

$$\Delta G = \Delta H - T\Delta S$$

<sup>4</sup> Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 34.

<sup>5</sup> Ambrose, Keulemans, and Purnell, *Analyt. Chem.*, 1958, **30**, 1582.

<sup>6</sup> Littlewood, Phillips, and Price, *J.*, 1955, 1480.

FIG. 4. *Heats of solution in cobalt stearate (kcal./mole). (For key see Fig. 1.)*

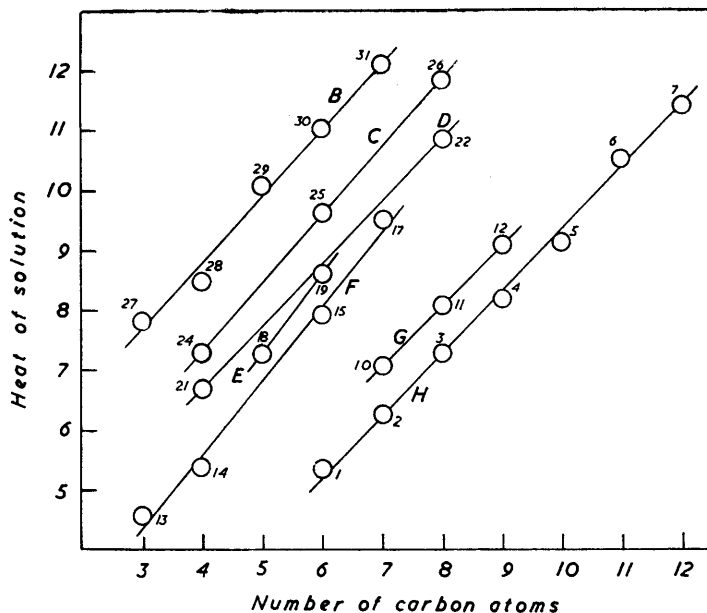
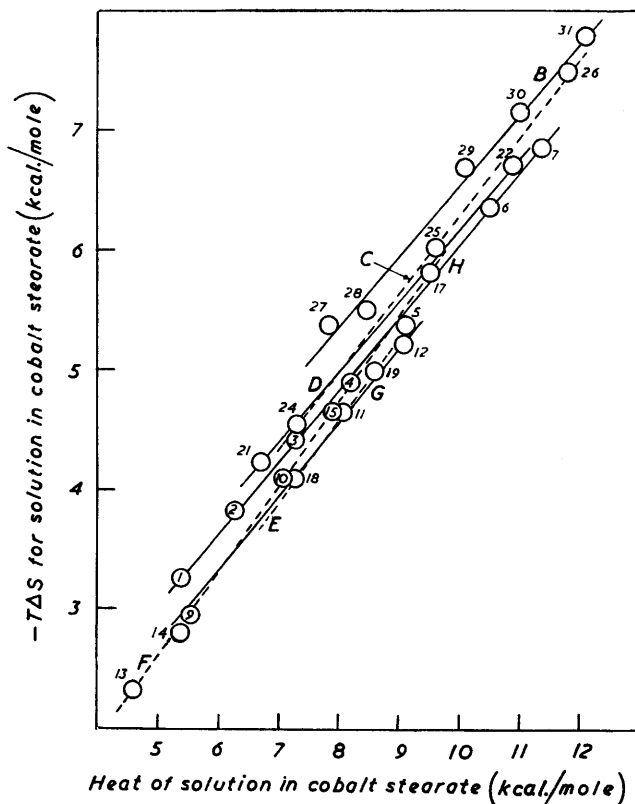


FIG. 5. *Relation between heats and entropies of solution in cobalt stearate. (For key see Fig. 1.)*



In calculating the entropies the approximation was made that the heat of solution at 156° was the same as the mean heat of solution over the range 110·6—156°. The free energies, heats, and entropies of solution will correspond to the transfer of 1 mole of the vapour to the solution in cobalt stearate from a volume in the gas phase which is the same as it will occupy in solution.

In each case a constant increment was found along any homologous series in  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  per  $\text{CH}_2$  group. Some heats of solution are plotted in Fig. 4. As has been noted in other solution studies,<sup>7</sup> there was a fairly linear relation between the heats and entropies of solution, as shown by Fig. 5. Excess heats of solution were calculated for some hydrocarbons and alcohols using heats of vaporisation extrapolated to 133° (mean of 110·6° and 156°) from values in Tables.<sup>8</sup> They were between 0·6 and 1·1 kcal./mole for hydrocarbons and of the order of 2 kcal./mole for alcohols, these values corresponding in each case to endothermic transfer from the pure solute to solution in cobalt stearate.

Some activity coefficients calculated for typical solutes in cobalt stearate at 156° are in Table 3.

TABLE 3. *Activity coefficients for solution in cobalt stearate at 156°*

Heptane .....	0·88	<i>m</i> -Xylene .....	0·59	Butyl alcohol ...	0·33	Diethylamine...	0·011
Octane .....	0·80	Mesitylene .....	0·55	Pentyl alcohol...	0·41	Triethylamine	0·15

We thank Imperial Chemical Industries Limited for the loan of recorders.

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<sup>7</sup> Bell, *Trans. Faraday Soc.*, 1937, **33**, 496.

<sup>8</sup> International Critical Tables.