The Chromatography of Gases and Vapours. Part III.* The Determination of Adsorption Isotherms.

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The paper shows how adsorption isotherms can be simply determined by the use of an apparatus designed for gas chromatography. To illustrate the method, the isotherms of benzene and *cyclo*hexane have been determined on charcoal at 77° and at 100°.

IN Part II * we described the construction of an apparatus for gas-chromatography, *i.e.*, chromatography in which the moving phase is a gas, and the use of this apparatus for the analysis of mixtures of volatile substances. The chromatographic methods depend upon repeated equilibrations between the moving gas and either a static liquid (partition) or a static solid surface (adsorption). The methods can therefore be used to give information about the equilibria involved, and it is the purpose of this paper to show how this may be done with particular reference to the determination of adsorption isotherms.

There are three basic chromatographic techniques, " elution," " displacement," and " frontal " analysis; each can be used to give information about the equilibria.

(i) *Elution Analysis.*—A sample of the substance is placed at the top of a suitable column, and is then carried down through the column in a slow stream of nitrogen or other inert gas. The sample eventually leaves the bottom of the column in the nitrogen stream, and its concentration is recorded (*e.g.*, by a thermal-conductivity cell) against time. The resulting record will approximate to one of the three types illustrated in Fig. 1. Type *A*, with a sharp concentration front and a trailing rear boundary, indicates an isotherm which curves towards the pressure axis (*e.g.*, Langmuir type). Type *B* indicates an isotherm curving away from the pressure axis, while the symmetrical Gaussian distribution of Type *C* indicates a linear isotherm. A simple elution experiment will thus show at once the type of isotherm involved.

Type *A* is generally the result of adsorption (*e.g.*, on charcoal or silica gel), although water vapour on charcoal at 20° behaves as Type *B* (Phillips, *Discuss. Faraday Soc.*, 1949, **7**, 241). Type *C* is produced by most of the partition columns, provided that the amount of sample used is not too great. As the quantity of sample is increased, the rear boundary sharpens (Type *B*), indicating a curvature of the isotherm away from the pressure axis at high concentrations. An example of this is given in Fig. 2. Fig. 3 illustrates the normal behaviour along a homologous series, where the curvature of the partition isotherm becomes more marked as the molecular weights rise.

With Type *C* the volume of nitrogen passed before the peak appears (retention volume) can be used to give an accurate value for the distribution coefficient of the substance between the gas and the liquid (Martin and Synge, *Biochem. J.*, 1941, **35**, 1358; Martin and A. T. James, *ibid.*, 1952, **50**, 679). An example illustrating the different solubilities of benzene and *cyclo*hexane in a number of solvents was given in Part II (*loc. cit.*).

(ii) *Frontal Analysis.*—The sample is carried on to the column continuously and at a constant concentration in a stream of nitrogen. For a substance having Type *A* behaviour the record is of a single sharp step, produced when the substance breaks through the column. From the time taken before the breakthrough the amount of the substance retained on the column can be determined. (For a mixture of such substances, a series of steps is produced, the number of steps being equal to the number of substances, and each step records the breakthrough from the column of a new component of the mixture.)

In order, therefore, to determine an isotherm point, nitrogen is saturated at a known temperature with the substance under investigation, and is then passed (suitably diluted

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* Part II, *J.*, 1953, 1600.

with more nitrogen where necessary) through a weighed quantity of adsorbent. The measurements required are flow-rate, weight of adsorbent, and the time of breakthrough. All these can be made simply and precisely. The sensitivity of the thermal conductivity cell (or other device), which actually records the breakthrough, need not be known, although the constancy of the step height produced on the recorder will be a check on the validity of the method. The only other information required is the vapour pressure of the substance at the saturator temperature. If this is not known, it may be determined as shown below, by displacement analysis.

The practical application of this technique to the determination of the isotherms of benzene and *cyclo*hexane on charcoal at 77° and 100° is given below.

(iii) *Displacement Analysis.*—The mixture to be analysed is placed on top of the column, and is then pushed through the column by means of a displacer vapour, which is
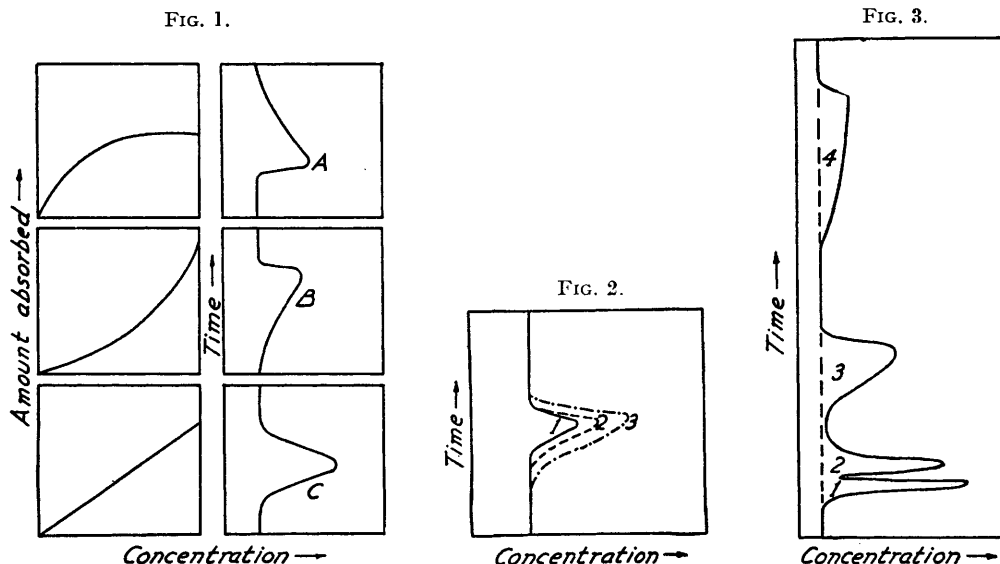
FIG. 1.

FIG. 2.

FIG. 3.

FIG. 1. *Typical elution analyses and related isotherms.*

FIG. 2. *Elution analyses, showing the effect of increased amounts of sample on the shape of the elution zone.*
   [Column : 1·5 ml. of Silicone 702, supported on Celite. Temp. : 56°. (1) 0·01 ml., (2) 0·02 ml., (3) 0·04 ml. of ethyl acetate.]

FIG. 3. *Elution analysis of a typical homologous series.*
   [Column : 1·5 ml. of tritolyl phosphate, supported on Celite. Temp. : 56°. 0·02 ml. each of (1) methyl acetate, (2) ethyl acetate, (3) propyl acetate, (4) butyl acetate.]

carried at constant concentration in a stream of nitrogen. This displacer must be more strongly adsorbed than any of the components of the mixture. Each component then forms a band of constant concentration on the column, and on leaving the column produces a step in the record of the thermal conductivity cell. When these bands have been established a component is adsorbed on a fraction of the column equal to the time its step eventually takes to leave the column (step length), divided by the breakthrough time of the displacer. The concentration of the vapour in equilibrium with the adsorbed component is the same as the concentration at which the step is formed, and may be simply calculated from the step length, the amount of the component in the mixture, and the nitrogen flow-rate. In this way an isotherm point can be established for each component of the mixture. By altering the nature of the displacer, or its concentration, other points can be determined.

It is to be noted that, as in the method of frontal analysis, the sensitivity of the thermal

conductivity cell is not important. In both methods only Type *A* systems can be satisfactorily studied, and only the ascending isotherm can be determined. No information can be obtained on hysteresis. The displacement method is not suitable in cases of irreversible adsorption.

The diplacement method can also be used for the determination of vapour pressures. Nitrogen, saturated at a known temperature with the substance whose vapour pressure is to be determined, is passed on to a column for a known time. It is then displaced, and the step length determined. This is then compared with a calibrated step obtained by using a known weight of the substance; *e.g.*, for benzene, *cyclo*hexane, and carbon tetra-chloride at 15° the ratio of the vapour pressure as determined to that recorded in the literature is 1·00, 0·99, 0·99, respectively.

EXPERIMENTAL

(i) *Apparatus.*—A block diagram of the apparatus is given in Fig. 4. The flow control *F* (James and Phillips, *J. Sci. Instr.*, 1952, **29**, 362), the saturator *S* and column *C* (*idem*, Part II, *loc. cit.*), and the thermal conductivity cell *TC* (Phillips, *loc. cit.*) have been described elsewhere.
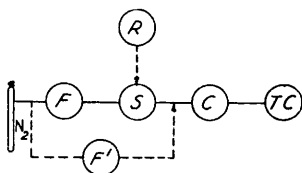
FIG. 4.

FIG. 5.

FIG. 4. *Block diagram of apparatus.*

  F Flow control.
  F' Subsidiary flow control for diluting the main vapour–nitrogen stream.
  S Saturator.
  R Pressure reducer.
  C Chromatographic column.
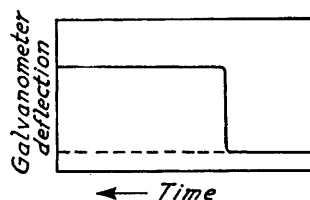 *TC* Thermal-conductivity cell.

FIG. 5. *Typical frontal analysis (record produced by the thermal conductivity cell).*

The only additional equipment used consisted of a pressure-reducer *R*, attached to the jacket of the saturator, to enable rapid changes of saturator temperature to be made without alteration of the jacketing liquid. This followed the design of Merriman and Wade (*J.*, 1911, **99**, 984), although more recently we have adopted a new design of our own (*J. Sci. Instr.*, in the press). A typical experimental result, *i.e.*, the record produced by the thermal conductivity cell, is shown in Fig. 5.

(ii) *Adsorbent.*—The charcoal used was the same as in the chromatographic analyses, reported in Part II (*loc. cit.*), *viz.*, Sutcliffe Speakman 208C. It was used in a granular form (B.S.S. 30—40) so that the pressure drop across the column was negligible. It was dried at 140° before use.

RESULTS AND DISCUSSION

Determination of the Adsorption Isotherms of cyclo*Hexane and Benzene on Charcoal, at 77° and at 100°, by Frontal Analysis.*—(i) *Calculation.* We use the following symbols : *P*, atmospheric pressure (mm. of Hg); *p*, vapour pressure of adsorbed substance (mm. of Hg) at the saturator temperature; *r*, nitrogen flow-rate into saturator (measured in ml. at room temperature and atmospheric pressure); *t*, breakthrough time (min.) of the substance; *g*, weight of adsorbent (g.); *T*, room temperature (°K); *S*, saturator temperature (°K).

In the following we shall assume that the vapours obey the ideal-gas laws. Reference to tables of generalised compressibility factors (Watson and Smith, *National Petroleum News*, July, 1936) indicates that for *cyclo*hexane and benzene, at the temperatures

concerned, deviations from these laws would lead to a correction of less than 1% at the highest vapour pressures we have used. In the determination of t, a correction was made for the dead volume of the apparatus. This was done by carrying out experiments with different amounts of charcoal in the apparatus. The correction was always less than 0·5 min.

In order to plot the isotherms, we require to know (*a*) the volume v of substance (corrected to S.T.P.) adsorbed per g. of column material at equilibrium, and (*b*) the partial pressure of the substance at the column temperature :

(*a*) v will be given by the relation (flow rate)(concentration of vapour) $\times t/g$, where the flow-rate which we need is the total flow-rate of nitrogen plus vapour leaving the saturator. This will be equal to $r(S/T)[P/(P - p)]$ ml./min. The concentration of vapour in this stream is $p/760$, so that, correcting to standard temperature, we get

$$v = 273rtPp/760gT(P - p) \text{ or } v = KtPp/gT(P - p)$$

(*b*) Although the temperature of the column is in most cases greater than that of the saturator, so that expansion takes place, the partial pressure of the substance will still be p, provided that the gas laws are obeyed. In this connection it is to be noted that the temperature difference between the column and the saturator is only large in the case of small vapour pressures.

(ii) *Results.* In all the experiments the flow rate r was constant at 43·0 ml./min., so the value for the constant K is 15·45. The results are given in Table 1.

TABLE 1.

P	p	T	g		v, ml.	P	p	T	g		v, ml.
		Benzene at 77°						*cyclo*Hexane at 77°			
765	5·70	297°	1·430	279	58·3	760	6·00	297°	1·610	178	34·8
765	26·70	297	1·730	85·6	71·2	762	27·55	297	1·730	54·4	46·7
765	61·55	297	1·440	33·5	81·0	762	63·00	297	1·620	24·3	53·5
765	158·0	297	1·476	13·0	91·3	762	160·0	297	1·580	9·02	60·2
765	262·5	297	14·50	64·7	93·1	762	245·0	297	14·40	49·2	64·0
765	401·1	297	15·90	34·7	95·7	760	360·0	297	15·10	28·1	66·3
765	586·4	297	14·45	10·7	96·2	760	540·8	298	14·90	10·2	67·0
		Benzene at 100°						*cyclo*Hexane at 100°			
753	26·70	297	1·760	74·0	60·6	762	27·55	297	1·740	46·8	40·1
755	58·20	298	1·430	29·5	67·5	762	63·00	297	1·660	21·7	46·7
758	158·9	298	1·280	9·75	79·6	762	160·0	297	1·380	7·20	55·0
765	262·5	298	15·90	67·5	87·8	762	245·0	297	14·60	45·0	57·9
765	424·8	298	14·94	27·5	91·1	760	360·0	297	15·32	26·6	61·9
765	596·0	298	16·00	10·7	93·3	760	540·8	297	15·55	10·4	65·2

(iii) *Discussion.* The isotherms are plotted in Fig. 6. In order to investigate more closely the nature of the adsorption, these results were replotted. Plots of $p/v(p_0 - p)$ against p/p_0 (where p_0 is the saturated vapour pressure at the column temperature), which should be linear for B.E.T. multimolecular adsorption, gave decided curves. Plots of p/v against p, which should be linear for unimolecular (or Langmuir) adsorption, gave good

TABLE 2.

		v_m		b					v_m		b	
		77°	100°	77°	100°				77°	100°	77°	100°
*cyclo*Hexane		68·0	67·1	0·037	0·032	Benzene	......		99·2	98·3	0·039	0·040

straight lines. These are shown in Fig. 7. From these plots the values of v_m and b of the Langmuir equation were calculated, and are given in Table 2. As the values of v_m are obtained from the slopes of the plots they are more certain than the values of b, which are obtained from the intercepts. The values of b enable a rough estimate of the heats of adsorption to be made. They are found to be of the order of 10 kcal./mole. More accurate values for the heats of adsorption were obtained from the values of p at equal surface coverages at 77° and at 100°. The average values so obtained were 10·4 for benzene and 7·8 kcal./mole for *cyclo*hexane.

We have also calculated the entropies of adsorption at 100°. These do not follow the simple R ln (area) law, suggesting that we have a case of localised adsorption, and we have therefore adopted Everett's procedure (*Trans. Faraday Soc.*, 1950, **46**, 942). Table **3** gives the values of the differential molar entropy ($\Delta \overline{S}\dagger$), and the calculated localisation entropies [R ln $\theta/(1 - \theta)$] for different values of θ, the fraction of the surface covered. The difference between these two entropies ($\Delta \overline{S}*$) should be a constant, and represents the loss of entropy on adsorption from a three-dimensional gas at 1 mm. pressure on to the half-covered surface. The average value for benzene is 35, and for *cyclo*hexane 28 entropy units. These values suggest that the motion of the benzene molecule is the more restricted.
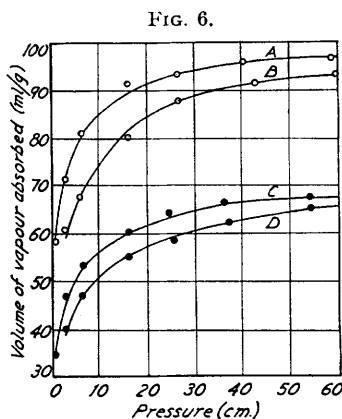

FIG. 6.

FIG. 7.

FIG. 6. *Adsorption isotherms*: *A*, Benzene at 77°. *B*, Benzene at 100°. *C*, *cyclo*Hexane at 77°. *D*, *cyclo*Hexane at 100°.
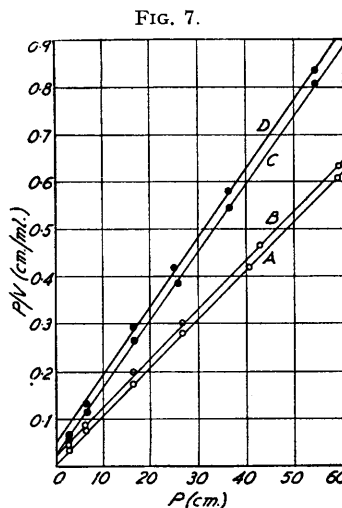
FIG. 7. *Adsorption isotherms, plotted according to the Langmuir equation.*

　　A, Benzene at 77°. *B*, Benzene at 100°. *C*, *cyclo*Hexane at 77°. *D*, *cyclo*Hexane at 100°.

TABLE 3.

θ	$\Delta \overline{S}\dagger$	R ln $\theta/(1 - \theta)$	$\Delta \overline{S}*$	θ	$\Delta \overline{S}\dagger$	R ln $\theta/(1 - \theta)$	$\Delta \overline{S}*$
		Benzene				*cyclo*Hexane	
0·62	35·7	1·1	34·6	0·60	27·3	0·9	26·4
0·69	37·0	1·6	35·4	0·70	29·2	1·7	27·5
0·81	38·1	3·0	35·1	0·80	30·8	2·8	28·0
0·89	38·9	4·3	34·6	0·85	31·7	3·5	28·2
0·93	39·9	5·1	34·8	0·90	32·1	4·4	27·7
0·95	40·5	5·9	34·6	0·97	34·0	6·2	27·8

A calculation following Kemball's procedure (*e.g.*, " Advances in Catalysis," Academic Press, New York, 1950, Vol. II, p. 233) gives a value of 32 entropy units for the adsorption as an ideal two-dimensional gas with unrestricted freedom of movement in two directions, and no freedom of movement in a direction perpendicular to the surface.