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AN IMPROVEMENT IN THE ELUTION TECHNIQUE FOR MEASUREMENT OF ADSORPTION ISOTHERMS BY GAS CHROMATOGRAPHY

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SUMMARY

The measurement of adsorption isotherms by the elution chromatographic technique and the application of a data logger and a computer for this purpose is described. A new method of calculation which commences from the top of the chromatographic peak and progresses downwards is developed. Long elution times are shown in the examples quoted but reproducible isotherms are obtained. Isothermic heats of adsorption calculated from these isotherms are found to be in better agreement with other methods of measurement than previous chromatographic results.

INTRODUCTION

The methods for the determination of adsorption isotherms by chromatographic techniques are divided into two types. Frontal analysis has been described by GREGG AND STOCK¹ and HABGOOD² and is based on the work of GLUECKAUF³. The slightly different technique of elution analysis was described by CREMER AND HUBER⁴ and has also been reviewed by HABGOOD² and SAINT-YRIEIX⁵. The first method would seem to be the more popular from a study of the literature, but is more difficult to carry out due to the difficulty of keeping the vapour at a constant partial pressure with a bubbler system or gas mixing device. The second method involving simple injection of a liquid sample with a syringe or gas with a dosing valve does not seem to have produced such successful results. The suitability of the elution method was therefore examined in this study.

EXPERIMENTAL

A conventional Pye 104 chromatograph was used with a separately heated katharometer detector. The apparatus was adapted so that parallel 10-cm columns made from 0.4-mm-bore pyrex glass tubing could be fitted using knurled nut type connectors with 'O' ring seals. These columns held about 1 g of sample. The carrier gas was helium which was dried by passing it over molecular sieve type 4A. The

two columns were packed with different samples, one acting as a blank while the other was being tested. Mercury manometers were added so that the pressure drop across the columns could be monitored and this was always kept below 100 mm of mercury height. The temperature of the columns was measured with a chrome-alumel thermocouple and was found to be constant to 0.01°C .

The output of the katharometer bridge was fed to a Solartron compact data logger which consisted of a digital voltmeter used on 20-mV range, coding circuits and a paper tape punch. A manual entry unit was also included to allow digits to be punched independently of the logger.

The katharometer reading was taken every 2 sec, coded and punched out on tape. At the end of a run the data tape was processed on an English Electric KDF9 computer to obtain the isotherm. The katharometer signal was simultaneously fed to a Kent Mark III potentiometer recorder on a 0–20 mV range as a visual check on the peak produced.

The katharometer was initially balanced to give a reading of about 0.18 mV on the digital voltmeter with the chromatograph attenuator set to an appropriate sensitivity. With the data logger running, an injection of $10\ \mu\text{l}$ was made in the normal type of septum cap and the polarity of output of the katharometer was reversed long enough for at least one negative reading to be punched and the polarity was then restored to positive. (This was to mark the injection time.) After the peak had appeared, ample time was allowed for the curve to return to the base line as seen on the chart paper and the digital voltmeter. The end of the data tape was then marked by punching the number 9999 using the manual entry unit. Certain control information for each run (described in the theory section) was also punched at the start of the tape using this unit. The data were logged as four digits (up to 2300 with the over-ranging allowed) without any decimal point indicated. A decimal point could, however, be entered in the control information section using the manual entry unit.

MATERIALS

In the results described here the adsorbent consisted of 1 g of a graphite occupying about 100 mm of the glass tube. The adsorbate was benzene and the adsorbent was held at temperatures near the boiling point of benzene. Flow rates were in the region of $20\ \text{ml min}^{-1}$. The katharometer was kept at 100°C so as to be always hotter than the columns. In later results a carbon black called spheron 9 was used.

THEORY

The theory to be described is based on the details given by SAINT-YRIEIX⁵ for results obtained on a normal chart recorder and is called here the old method.

Correction of diffusion

Following the method given by BECHTOLD⁶ the diffusion in front of a peak was assumed to be equal to the diffusion to the rear of a peak at each concentration level. This is shown in Fig. 1, the distances x on the front of the peak being subtracted from the rear portion of the curve at each concentration level.

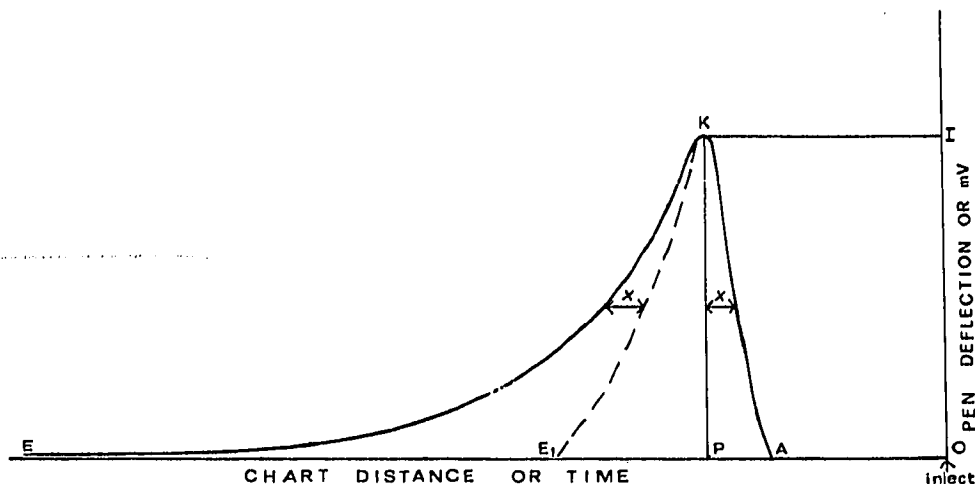


Fig. 1. The correction of the tailing edge of a chromatographic peak for diffusion.

A point on the adsorption isotherm $f(C_1)$ may then be calculated using the formula:

$$f(C_1) = \frac{WQ}{ug} \int_0^{n_1} (l - l_0) dn \tag{1}$$

where W is the carrier gas flow rate ($\text{cm}^3 \text{sec}^{-1}$), Q the sensitivity of the detector given by C/n and assumed to be a constant ($\mu\text{mole cm}^{-4}$), C the concentration of the adsorbate in the gas phase, usually in $\mu\text{mole cm}^{-3}$; n the deviation of the chart pen from the base line (cm), u the speed of the chart paper (cm sec^{-1}), g the mass of the adsorbent (g), l the distance on the chart paper from the injection point to a particular point on the curve (cm), l_0 the distance on the chart paper from the injection point to the appearance of a non-adsorbed gas such as air (cm).

With the size of columns being used in this experiment l_0 was found to be zero and was neglected. Fig. 2 shows the meaning of this integral on a typical experimental

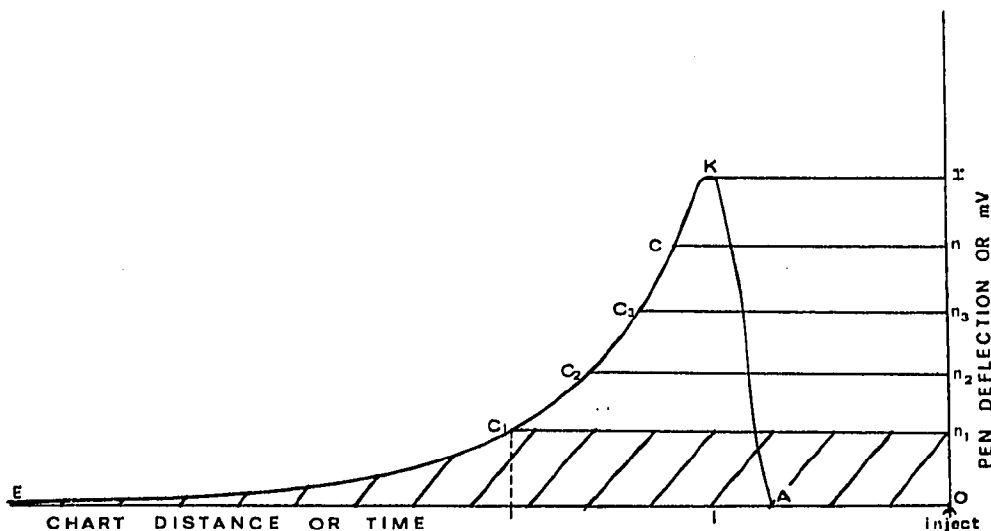


Fig. 2. The calculation of adsorption values from a chromatographic peak.

curve. The point with deviation n_1 from the base line is at a distance l from injection, thus the shaded area represents the integral and multiplication by the other factors of eqn. 1 gives one point on the isotherm. The concentration at which this amount is adsorbed is given by

$$C_1 = Qn_1 \quad (2)$$

Further points on the isotherm are then obtained by drawing more horizontal lines at say n_2, n_3 etc. and adding on the extra areas then included. The calculation is thus carried up the experimental curve from the base line to the peak. The number of such points obtained is governed by the tedium of dividing the diagram by a large number of lines and estimating areas. The areas may be found by counting squares or similar methods but more commonly the horizontal lines are assumed to be close enough together to assume that the portion of the curve cut off between two lines approximates to a straight line. The area is then a trapezium and its area is the difference between deviations n for the upper and lower lines times the average value of l . A reasonable number of lines to draw in this method would be about twenty. The value of Q is obtained by what is effectively a simultaneous calibration. The amount of solute injected is proportional to the area under the curve for any chromatographic peak. The area under the whole peak in Fig. 1 was found (before diffusion correction) and is called S . If the amount of solute injected is m μ moles, then:

$$Q = \frac{um}{WS} \quad (3)$$

where

$$S_1 = \int_{l_1}^{l_2} n dl \quad (4)$$

Use of the data logger to investigate the old method of calculation

Eqn. (1) may be rewritten (dropping l_0) as

$$f(C_1) = \frac{WQ}{g} \int_0^{n_1} \frac{l}{u} dn = \frac{WQ}{g} \int_0^{n_1} t dn \quad (5)$$

where t is the time of the particular point after injection and n now represents the digital voltmeter reading above the base line reading instead of cm of chart paper.

Similarly in eqn. 3 dividing S by u gives an area S_1 in terms of time \times voltmeter reading,

$$Q = \frac{m}{WS_1} \quad (6)$$

where

$$S_1 = \int_{t_1}^{t_2} n dt \quad (7)$$

The absence of the decimal point in the reading punched out does not matter

because the value of n appears in the calibration in eqn. (7) as well as in eqn. (5). Combining eqns. (6) and (5) gives

$$f(C_1) = \frac{m}{S_{1g}} \int_0^{n_1} t \, dn = Q_2 \int_0^{n_1} t \, dn \quad (8)$$

where $Q_2 = m/S_{1g}$ is a constant factor. The value of C_1 is obtained from eqn. 2 in $\mu\text{mole cm}^{-3}$ (n_1 is now voltmeter reading).

Assuming ideal gas behaviour of the vapour

$$P = CRT$$

where P is pressure

$$\therefore P = RTQn_1 = 8.31 \times 10^{-3} TQn_1 \text{ in kN m}^{-2}$$

The quantities m , g , W and T were entered on the data tape at the start of a run.

The reading was logged at regular 2-sec intervals so as the data were read into the computer an integer representing time was increased by two as each piece of data was read in and stored as the time of that piece of data. This time sequence was only started from zero after the negative reading representing injection had been detected.

Since a large number of points on the experimental curve are read into the computer (several hundred) a more complete and more accurate isotherm results. It would be pointless to allow the computer to print out all these points, so since they were relatively closely spaced along the isotherm the points were used to interpolate for the pressure at which standard amounts of material are adsorbed. The steps were chosen this way round to ease the calculation of isosteric heats of adsorption. The points chosen were 5, 10 and 20 $\mu\text{mole g}^{-1}$ and steps of 20 $\mu\text{mole g}^{-1}$ up to the peak of the curve (highest point on the isotherm obtained from that experiment).

The main difficulty in conducting this experiment was to detect when the recording device had returned to the base line. Since base line drift could and did occur, this had necessarily to be a return to a constant reading and not to the original reading before the peak. The digital voltmeter proved to be more sensitive than the pen recorder but due to inherent noise in the output of the katharometer the last digit tended to wander up and down while reaching a final constant value. The shape of the curve for benzene on carbon showed a large degree of tailing (steep isotherm at low pressures) and a pronounced asymptotic approach to the base line. This made detection of the finishing point very difficult. Unfortunately this point needs to be known accurately to allow the start of the integrations implied in eqn. 5. A special numerical procedure to find this point had to be adopted.

If all the data logged in the asymptotic region are examined it is seen to involve a large number of readings changing only very slowly by one in the last digit, constant readings or even rising readings for a few steps. Thus a simple comparison of the digits of a pair of successive readings is of no use nor is a smoothing procedure trustworthy in this case (SAVITSKY AND GOLAY⁷). The processing program was arranged to store every separate reading until the rear portion of the peak was appearing and

a pair of readings remained constant. The first reading was stored normally with the previous ones, but the second was stored in a separate loop of the program with the first reading repeated as well. The following readings were stored in this sub-section and a running average of these readings was computed. This average value was compared with the last reading in the main storage array until twice the difference between them equalled or exceeded unity. This means that despite fluctuations in actual readings taken, on average a decrease of unity in the last digit has been detected. The last figure stored in the main array and the average were then used to calculate a new figure for the main array (twice the average minus last stored reading). The time continued to increase as each figure was read in but only the last time was stored to correspond to the new array figure. The figures stored in the array thus continued to decrease by about unity but the time scale stretched out more and more as the slope became less. This procedure economised on storage space and computing time by reducing the stored data to reasonable proportions. All the data stored were then used in subsequent calculations. The end of the data tape was detected when the 9999 previously added as a marker was reached.

The integration involved for eqns. 7 (calibration) and 8 (isotherm points) was then carried out numerically by the computer.

RESULTS AND DISCUSSION

To test the reproducibility of the method duplicate injections of 10 μl of benzene were made under fixed conditions. The results are shown in Table I and were obtained with elapses of 1 h and 24 h between injections. A second injection about 1 h after the first produced a higher peak (up to 10 % higher) as did injections at 2-h and 8-h intervals. The best reproducibility of peak heights as seen on the recorder was obtained after purging for 24 h. It was assumed that the last of the benzene requires 24 h to be purged off a column despite the apparent return of the trace to the baseline. Thus readings are best only taken at 24-h intervals.

TABLE I

REPEATABILITY OF AN ISOTHERM USING THE OLD METHOD OF CALCULATION

Adsorption of benzene on graphite at 345° K. Detector sensitivity setting 10. Flow rate at katharometer temperature, 28.0 ml min⁻¹. Flow rate at column temperature, 25.5 ml min⁻¹. Area under the curve, 3.207 × 10⁶. Lowest point on the isotherm, 0.97 $\mu\text{mole g}^{-1}$ at 0.0025 kN m⁻².

Adsorption ($\mu\text{mole g}^{-1}$)	Pressure (kN m ⁻²)	ln (pressure)	Difference between two injections			
			Pressure		ln (pressure)	
			1 h	24 h	1 h	24 h
5	0.001	-4.312	0.011	0.003	0.595	0.259
10	0.003	-3.536	0.022	0.006	0.564	0.220
20	0.007	-2.673	0.004	0.010	0.493	0.153
40	0.185	-1.686	0.087	0.014	0.383	0.076
60	0.353	-1.041	0.128	0.013	0.310	0.038
80	0.577	-0.551	0.172	0.009	0.261	0.015
100	0.863	-0.147	0.220	0.001	0.227	0.001
120	1.225	0.203	0.277	0.012	0.204	0.009
140	1.682	0.520	0.348	0.032	0.188	0.018
160	2.267	0.819	0.435	0.061	0.175	0.026

The results in Table I show clearly the improvement in reproducibility of 24-h injections over 1-h interval injections at least at the upper end of the isotherm. Experiments at 354°K and 344°K gave the isosteric heats of adsorption shown in Table II. The heat of condensation of benzene is 30.7 kJ mole⁻¹ so the low values for heat of adsorption shown at the low pressure end are unexpected and do not compare with results obtained by static adsorption measurements³. The results are, however, similar to those of CREMER AND HUBER⁴. It was then assumed from the slow elution shown above and the unreasonably low heats of adsorption produced that some benzene is eluted too slowly to be detectable in the katharometer. Since the calculation of the isotherm starts from the point of return to the base-line with the assumption of zero adsorption the whole of the isotherm must be seriously in error. It should be noted that the value of S_1 and thus of Q is also incorrect.

TABLE II

VARIATION OF \ln (PRESSURE) WITH AMOUNT ADSORBED AT TWO TEMPERATURES AND HEAT OF ADSORPTION — ΔH

Adsorption ($\mu\text{mole g}^{-1}$)	\ln (pressure)		$-\Delta H$ (kJ mole ⁻¹)
	at 354° K	at 344° K	
5	-3.771	-3.865	7.1
10	-2.989	-3.068	8.0
20	-2.043	-2.199	15.9
40	-0.912	-1.156	14.6
60	-0.160	-0.450	29.7
80	0.408	0.094	31.8
100	0.867	0.537	33.4
120	1.256	0.914	34.7
140	1.596	1.245	35.6
160	1.901	1.543	36.4

The new method of calculation

To overcome this difficulty a method of estimating the error at the bottom of the isotherm is required or the calculation of the isotherm from the top downwards must be made. The second of these alternatives was attempted firstly by obtaining an independent value of S_1 and thus of Q . Since the method assumes linearity of the detector the area under the peak S_1 is proportional only to the amount injected and is independent of peak shape. Thus other column packings may be used which produce a sharper return to base line. At first other solid adsorbents were tried, but the best results were obtained using a standard 1-m column packed with 15% Silicone SE-30 on Celite.

This was operated at the same temperature of detector and flow rate as in the adsorption experiment. The value of S_1 obtained was dependent upon flow rate, despite parallel flow in the detector, *i.e.* both halves at atmospheric pressure. Since, in the adsorption run, the flow rate could not be reset accurately, but had to be read each time, calibrations were carried out at various flow rates and a calibration graph was drawn to give the correct S_1 at any flow rate. The reproducibility of S_1 using the liquid column at constant flow rate is shown in Table III and compared with values obtained on solid columns with severe tailing and non-elution of residual

benzene. The variation of S_1 with flow rate used to produce a calibration graph is also shown in Table III.

In the adsorption calculations the correct S_1 is read in with the initial data and used to calculate Q , Q_1 and pressure values using eqn. 2. In Fig. 2 the maximum adsorption is given by the area EKIO, but it is now assumed that there is an error at E and that area EKA is incorrect and should be obtained from S_1 .

In Fig. 1 the area E_1KA represents S_1 which is the required area EKA plus the strip E_1KE . Since the distances marked x are equal this strip is equal in area to PKA. Using the points along the curve AK and dividing into horizontal strips a numerical integration for PKA was obtained. This was subtracted from S_1 to obtain area EKA and to this was added area AKIO also obtained by numerical integration, the total being the required area EKIO.

TABLE III

REPEATABILITY OF AREA UNDER THE CURVE ON A LIQUID COLUMN

Liquid column, 15 % silicone SE-30 on Celite. Sample injected, 10 μ l benzene. Detector sensitivity, 50. Column temperature, 364.7°K; katharometer temperature, 373.9°K. Flow rate at katharometer temperature, 14.4 ml min⁻¹. Calibration of katharometer at various flow rates. Flow rates given at katharometer temperature. Flow rates, 32.5, 34.4, 31.3, 24.7, 19.5, 17.9, and 15.8. Area $\times 10^{-4}$, 3.502, 3.242, 3.534, 4.515, 5.902, 6.485 and 7.253 (logged reading \times sec).

No. of run	Area $\times 10^{-4}$ (logged reading \times sec) on liquid column
1	6.938
2	6.907
3	6.913
4	6.912
5	6.708
6	6.844
7	6.889
8	6.926
9	6.959

TABLE IV

REPEATABILITY OF AN ISOTHERM USING THE NEW METHOD OF CALCULATION

Lowest point detected on the isotherm, 19.93 μ mole g⁻¹ at 0.002 kN m⁻². Amount not desorbed at the end of calculation (pressure appears to be zero), 19.13 μ mole g⁻¹. Conditions, as in Table I. Area under curve taken from calibration data, 3.90 $\times 10^6$.

Adsorption (μ mole g ⁻¹)	Pressure (kN m ⁻²)	ln (pressure)	Difference between two injections			
			Pressure		ln (pressure)	
			1 h	24 h	1 h	24 h
5	—	—	—	—	—	—
10	—	—	—	—	—	—
20	0.0022	-6.109	—	0.0003	—	0.132
40	0.078	-2.545	0.027	0.007	0.298	0.097
60	0.214	-1.543	0.064	0.009	0.261	0.040
80	0.414	-0.882	0.102	0.005	0.220	0.012
100	0.688	-0.374	0.147	0.003	0.194	0.004
120	1.052	0.051	0.205	0.016	0.078	0.014
140	1.538	0.430	0.283	0.036	0.017	0.023

TABLE V

HEATS OF ADSORPTION OF CYCLOHEXANE ON SPHERON 9 CALCULATED FROM ISOTHERMS AT 348.7°K, 351.1°K, 355°K, 360°K, AND 365°K

Adsorption ($\mu\text{mole g}^{-1}$)	$-\Delta H$	
	kcal mole^{-1}	kJ mole^{-1}
5	11.4	47.9
10	9.6	40.3
20	10.2	42.6
40	8.5	35.7
60	8.5	35.7
80	8.5	35.7
100	8.5	35.7
120	8.5	35.7
140	8.5	35.7
160	8.5	35.7
180	8.5	35.7
200	8.5	35.7
220	8.5	35.7
240	8.5	35.7
260	8.5	35.7

The other points on the isotherm were then obtained by subtracting successive trapezia KInC until the base line was reached. The residual amount adsorbed at this point was found to be of the order of 10–20 $\mu\text{mole g}^{-1}$.

The reproducibility of the isotherm by this new method is shown in Table IV using exactly the same data as for Table I. The results are better or at least as good as the old method but terminate at about 20 $\mu\text{mole g}^{-1}$ because this amount is not eluted at a measurable concentration. The more reasonable values of heat of adsorption are shown in Table V and further results in Figs. 3 and 4.

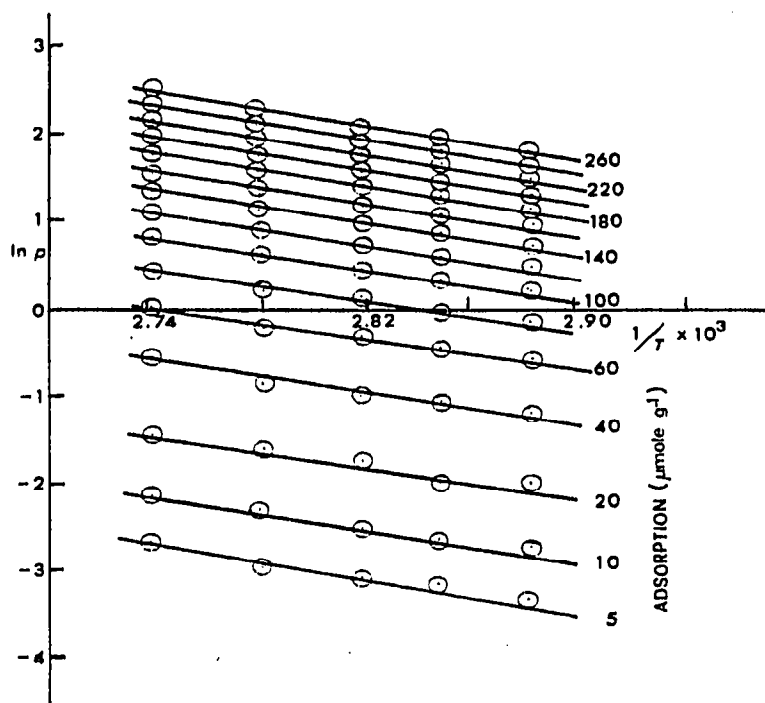


Fig. 3. Plots of $\ln P$ against $1/T$ at various coverages of cyclohexane on spheron 9.

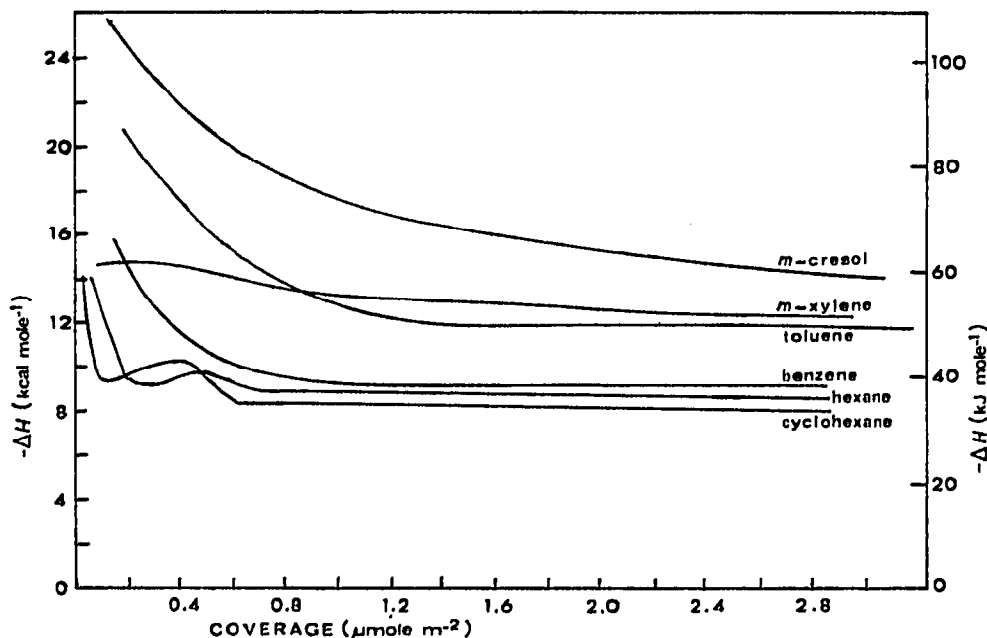


Fig. 4. Variation of $-\Delta H$ with coverage for spheron 9 and various adsorbates.

CONCLUSIONS

The elution technique for the measurement of the initial part of adsorption isotherms has proved to be very simple to carry out with standard chromatographic equipment. The tedious calculation involved is relieved by the use of a data logger and a computer. The change in the method of calculation produces more meaningful results for heat of adsorption at low coverage showing good correlation over a range of temperatures. A lower limit of adsorption measurements of $10\text{--}20 \mu\text{mole g}^{-1}$ is also shown for a sample of about $100 \text{ m}^2\text{g}^{-1}$ surface area.

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REFERENCES

- 1 S. J. GREGG AND R. STOCK, in D. H. DESTY (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, p. 90.
- 2 H. W. HARGOOD, in E. A. FLOOD (Editor), *The Solid-Gas Interface*, Vol. II, Arnold, London, 1967, pp. 611-846.
- 3 E. GLUECKAUF, *J. Chem. Soc.*, (1947) 1302; *Nature*, 156 (1945) 748; *ibid.*, 160 (1947) 301.
- 4 E. CREMER AND H. F. HUBER, *Angew. Chem.*, 73 (1961) 461.
- 5 A. SAINT-YRIEIX, *Bull. Soc. Chim. France*, (1965) 3407.
- 6 E. BECHTOLD, in M. VAN SWAAY (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 49.
- 7 A. SAVITSKY AND M. J. E. GOLAY, *Anal. Chem.*, 36 (1964) 1627.
- 8 A. A. ISIRIKYAN AND A. V. KISELEV, *J. Phys. Chem.*, 65 (1961) 601; *ibid.*, 66 (1962) 210.