

A STUDY OF THE EVAPORATION OF THE STATIONARY PHASE FROM GAS-LIQUID CHROMATOGRAPHIC COLUMNS

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Besides a high selectivity, two fundamental requirements for a stationary phase used in gas-liquid chromatography are its thermal stability and low volatility under operating conditions. These two properties of the phase determine the reproducibility of the specific retention volumes and base line stability as well as the life time of the column.

The thermal stability of any particular phase (if we assume a catalytically inactive inert support) is well defined by the temperature of its degradation.

The problem concerning the evaporation of the phase, however, is more complicated since in this case several factors can have a simultaneous influence.

An experimental investigation of this problem would provide data, which might be used as a reasonable basis for a quantitative assessment of the suitability of phases for the conditions of the experiment.

A few data have been published up to date about the evaporation of the liquid phases. Most¹⁻⁴ concern only one influencing parameter and are not connected with any mathematical expression.

AMBROSE AND AMBROSE⁵ suggest a formula for liquid phase evaporation, but give no experimental data concerning its validity.

The present study was undertaken as an attempt to explore in a more systematic and complete way the evaporation of the liquid phase and to suggest a convenient expression, based on experiments, for some calculations.

EXPERIMENTAL

All measurements were carried out with an apparatus which was a somewhat simplified model of a gas chromatograph without its detecting and recording systems.

Pure dry nitrogen was used as carrier gas. Its inlet pressure was reduced by means of coarse and fine reducing valves. The outlet flow rate was measured with a soap flowmeter at the end of the column.

The temperature of the chromatographic column enclosed in an air thermostat was controlled to within $\pm 1^\circ$.

The column employed was a 50 cm glass U-shaped tube with 4 mm internal diameter. The inlet part of the column (about 1/3 of its length) was always filled with glass spheres (1 mm diam.). Thus the nitrogen was preheated to the column temperature before entering the chromatographic packing.

Ground unglazed tile with particle size diameter 0.2–0.4 mm was used as solid support.

In all measurements di-*n*-propyl phthalate was used as stationary phase. The weight of the latter was 10 % of the weight of the chromatographic packing. The packing was prepared as one lot for all experiments.

The evaporation of the stationary liquid was checked by means of the weight of the column, with an accuracy of ± 0.0001 g. For that reason every column packing was weighed before filling, and the column was weighed before, during (if necessary) and after the experiment.

In order to avoid errors due to evaporation of solvent traces, humidity or other compounds of low volatility, before each experiment the column was left under operating conditions for 15 min, then weighed, and the stationary phase losses were measured from this moment.

In the present work we investigated the influence of the following factors on the evaporation of the stationary phase from the column: volume of the carrier gas passes through the column and column temperature.

RESULTS AND DISCUSSION

Dependence of the total quantity of the stationary phase evaporated on the volume of gas passed through the column

The evaporation of the stationary phase, depending on the volume of gas passed through the column, was investigated at 100° and with a nitrogen flow rate of 120 ml/min.

Every half hour the column was disconnected, weighed on an analytical balance and then reconnected to the apparatus. These periodic measurements were continued until the stationary phase was completely evaporated (the initial weight was 0.3734 g).

The data for the quantity of the evaporated stationary phase, depending on the time or on the volume of gas passed through the column are shown in Table I.

As is evident from Fig. 1, in which the data shown in Table I are presented graphically, the total quantity of the evaporated phase is a linear function of the volume of gas passed through the column. This function might therefore be expressed by the equation

$$m = A \cdot V \quad (1)$$

where m is the quantity of the stationary phase evaporated from the column and V is the volume of gas passed through it. The coefficient A is actually the concentration of the stationary phase vapours in the eluent gas at the end of the column. Its value in the present case, found by the method of least squares without the last two points, is $2.75 \cdot 10^{-6}$ g/ml.

The data in Table I show that the concentration of the stationary phase in the eluent gas does not depend on the total quantity of the phase in the column. On the other hand these data are in accordance with the assumption that the saturation of the gas with vapour is reached very quickly and takes place in a narrow section near the column inlet.

From the curvature at the end of the line in Fig. 1 (the last two points), where the concentration of the phase decreases and the gas leaves the column before satu-

TABLE I

DEPENDENCE OF THE EVAPORATION, AT 100°, OF THE STATIONARY PHASE ON THE VOLUME OF GAS PASSED THROUGH THE COLUMN

Sample No.	Time (h)	Gas volume (ml × 10 ⁻³)	Amount of liquid phase evaporated	
			g	%
1	0.5	3.6	0.0101	2.7
2	1.0	7.2	0.0198	5.3
3	1.5	10.8	0.0294	7.9
4	2.0	14.4	0.0396	10.6
5	2.5	18.0	0.0493	13.2
6	3.0	21.6	0.0601	16.1
7	3.5	25.2	0.0706	18.9
8	4.0	28.8	0.0800	21.4
9	4.5	32.4	0.0896	24.0
10	5.0	36.0	0.0993	26.6
11	5.5	39.6	0.1087	29.1
12	6.0	43.2	0.1184	31.7
13	6.5	46.8	0.1292	34.6
14	7.0	50.4	0.1393	37.3
15	7.5	54.0	0.1497	40.1
16	8.0	57.6	0.1587	42.5
17	8.5	61.2	0.1714	45.9
18	9.0	64.8	0.1781	47.7
19	9.5	68.4	0.1878	50.3
20	10.0	72.0	0.1968	52.7
21	10.5	75.6	0.2072	55.5
22	11.0	79.2	0.2162	57.9
23	11.5	82.8	0.2263	60.6
24	12.0	86.4	0.2360	63.2
25	12.5	90.0	0.2468	66.1
26	13.0	93.6	0.2580	69.1
27	13.5	97.2	0.2674	71.6
28	14.0	100.8	0.2774	74.3
29	14.5	104.4	0.2883	77.2
30	15.0	108.0	0.2972	79.6
31	15.5	111.6	0.3077	82.4
32	16.0	115.2	0.3178	85.1
33	16.5	118.8	0.3293	88.2
34	17.0	122.4	0.3398	91.0
35	17.5	126.0	0.3499	93.7
36	18.0	129.6	0.3596	96.3
37	18.5	133.2	0.3663	98.1
38	19.0	136.8	0.3716	99.4
39	19.5	140.4	0.3730	99.9

ration, it is possible to calculate that the section mentioned above contains about 2 % of the stationary phase and represents 2% of the active column length. As the latter was 25 cm, the saturation section was 0.5 cm long.

The size of the saturation section will depend on the gas flow rate and on the nature and particle size diameter of the inert support. In the case of usual gas chromatographic practice, however, the length of the saturation section will always be many times shorter than the total length of the column packing and *A* must not show any dependence on the flow rate. This is illustrated by the data in Table II, which

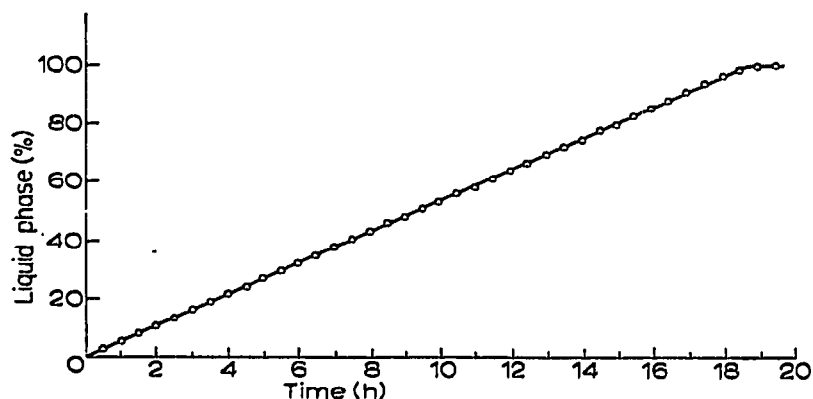


Fig. 1. Percentage of the evaporated liquid phase depending on the volume of gas passed through the column.

show the values of the phase concentration in the eluent gas at 100°, with different velocities of carrier gas.

It is evident from the data in Table II that for the gas velocities most frequently used in gas-liquid chromatography the concentration remains practically constant.

TABLE II

CONCENTRATION OF THE STATIONARY PHASE IN THE ELUENT GAS AT DIFFERENT GAS VELOCITIES

Sample No.	Gas flow rate (ml/min)	Gas volume passed through the column (ml)	Concentration <i>A</i> (g/ml × 10 ⁶)
1	20	1200	3.1
2	40	2400	3.1
3	60	3600	2.4
4	80	4800	2.5
5	100	6000	2.8
6	120	7200	2.7
7	150	9000	2.6

Influence of the temperature on the evaporation of the liquid phase

The influence of the temperature on the evaporation of the liquid phase was investigated at 80°, 100°, 120° and 140°, and with a gas flow rate of 60 ml/min.

Table III shows the values of the vapour concentrations of the stationary phase in the eluent gas at the temperatures under investigation.

It can be seen in the present case that the dependence $A = f(T)$ (Fig. 2) is similar to the well known dependence between the saturated vapour pressure and the temperature.

On the other hand, if we take into consideration that the concentration of the stationary phase vapour in the eluent gas is in direct proportion to the saturated vapour pressure, it is to be expected that the expression

$$\ln A = -\frac{H_v}{RT} + C \quad (2)$$

which is a modified form of the Clausius-Clapeyron equation, will be applicable to the data in Table III.

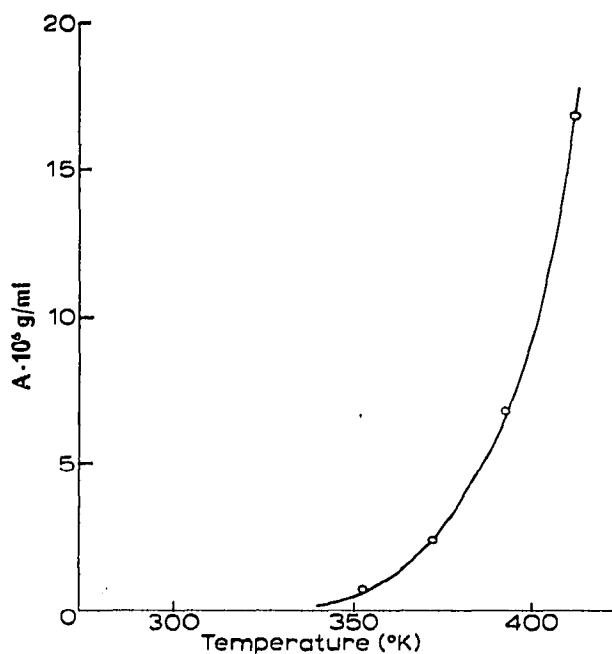


Fig. 2. Concentration of the liquid phase vapours in the eluent gas as a function of temperature.

In eqn. (2) A has the same meaning as in eqn. (1), T is the temperature in °K, H_v is the molar latent heat of vaporization and C is a constant.

It was found that the data in Table III, plotted as $\log A = f(1/T)$, lie on a straight line (Fig. 3), which confirms our assumption about the applicability of eqn. (2).

TABLE III

CONCENTRATION OF STATIONARY PHASE IN THE ELUENT GAS AT DIFFERENT TEMPERATURES

Sample No.	Temperature (°K)	Concentration A (g/ml $\times 10^6$)
1	353	0.9
2	373	2.8
3	393	7.0
4	413	16.5

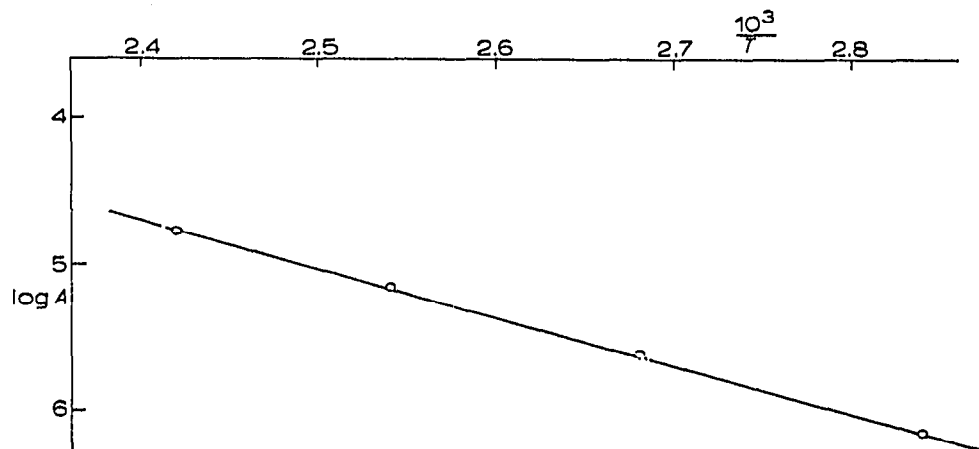


Fig. 3. Plot of the logarithm of the phase vapour concentration in the eluent gas vs. the inverse of the temperature.

The value of the molar latent heat of vaporization found mathematically is -13.638 kcal/mol. Hence the equation of the straight line in Fig. 3, over the range of conditions investigated, will be:

$$\log A = \frac{-13.638}{2.3 RT} + 2.427 \quad (3)$$

A general expression for the evaporation of the stationary phase from a GLC column

Since the eluent gas in a gas chromatography column becomes fully saturated with the vapour of the stationary phase, three factors determine the evaporation, *viz.* the specificity of the phase, the volume of gas passed through the column, and the temperature.

In accordance with the experimental data shown above, a more general equation was obtained:

$$\ln m = -\frac{\Delta H_v}{RT} + \ln V + C \quad (4)$$

where the symbols m , T , ΔH_v , V and C have the same meaning as in the previous equations.

Equation (4) permits calculation of the liquid phase losses, or the vapour concentration of the stationary phase in the eluent gas flow, if ΔH_v , T , V and C are known.

Hence it would be useful to have tables with the values of ΔH_v and C for the most important phases. This would provide a quantitative basis for liquid phase characterization from the viewpoint of the experimental conditions.

Table IV shows the amount of the evaporated liquid phase found experimentally and by calculation with the help of eqn. (4) at different temperatures and gas volumes.

TABLE IV

QUANTITY OF THE LIQUID PHASE EVAPORATED FROM THE COLUMN FOUND EXPERIMENTALLY AND BY CALCULATION

Sample No.	Temperature ($^{\circ}K$)	Gas volume (ml)	Liquid phase evaporated		Δm
			Found	Calculated	
1	373	36000	0.0993	0.0986	-0.0007
2	373	90000	0.2468	0.2464	-0.0004
3	373	126000	0.3499	0.3450	0.0001
4	353	3600	0.0032	0.0033	0.0001
5	373	3600	0.0099	0.0099	0.0000
6	393	3600	0.0252	0.0258	0.0006
7	413	3600	0.0594	0.0588	-0.0006

Equation (4) permits ready determination of the value of the molar latent heat of vaporization for a high boiling organic liquid. Thus if the same gas volume V is passed through a column at two different temperatures and liquid phase losses are found to be m_1 and m_2 , then

$$\Delta H_v = \frac{2.3 RT_1 T_2 \log (m_1/m_2)}{T_1 - T_2} \quad (5)$$

The apparatus and techniques of measurement are very simple and the determination can be carried out in most laboratories.

This method for determination of the molar latent heat of vaporization by means of GLC is applicable to compounds of low volatility, in contrast to the method of MACKLE, MAYRICK AND ROONEY⁶.

SUMMARY

The present work is an attempt to investigate the evaporation of the liquid phase from gas-liquid chromatography columns.

A general expression for the quantity of the evaporated liquid phase depending on its nature, on the gas volume passed through the column and on the temperature was found. At the same time a method for the determination of the molar latent heat of vaporization of high boiling compounds is suggested.

It is thought that a quantitative characterization of the phases from the viewpoint of the experimental conditions is possible on the basis of tabulated data for the two constants of the equation found in the work.

REFERENCES

- 1 S. J. HAWKES AND E. F. MOONEY, *Anal. Chem.*, 36 (1964) 1473.
- 2 S. T. PRESTON, JR., *J. Gas Chromatog.*, 1 (1963) 8; *C.A.*, 56 (1963) 5811f.
- 3 S. DAL NOGARE AND W. E. LANGLOIS, *Anal. Chem.*, 32 (1960) 767.
- 4 W. GERRARD, S. J. HAWKES AND E. F. MOONEY, in R. P. W. SCOTT (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, pp. 263-271.
- 5 D. AMBROSE AND B. AMBROSE, *Gas Chromatography*, George Newnes, London, 1961, pp. 98-100.
- 6 H. MACKLE, R. G. MAYRICK AND J. J. ROONEY, *Trans. Faraday Soc.*, 56 (1960) 115.

J. Chromatog., 30 (1967) 332-338