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A MODIFIED GAS CHROMATOGRAPH FOR THERMODYNAMIC MEASUREMENTS BY FRONTAL CHROMATOGRAPHY

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SUMMARY

A technique is described for producing finite concentration thermodynamic data by means of a modified commercial gas chromatograph. The theory involved and the computerized data handling system are discussed. The technique is favorably compared with static data for the system *n*-hexane in *n*-hexadecane at 30 °

INTRODUCTION

The normal elution form of gas chromatography has been used successfully for many years to measure the infinite dilution thermodynamic mixing properties of chromatographic systems. The two primary limitations of the elution mode are: (1) solutions can be studied only when the solute concentration approaches zero, and (2) the solute and solvent must be suitable for chromatography. That is, the solute must be volatile at the temperature of the experiment, while the solvent must be relatively non-volatile, pure, and stable. The advantages of elution chromatography are numerous, and some of the most important of these are: (1) simplicity of the apparatus and theory, (2) wide temperature range, (3) rapid data acquisition rate, (4) very accurate and reproducible data at low concentration, and (5) direct measurement of thermodynamic data in the infinite dilution range which is usually accessible only by extrapolation from the finite concentration range. Because of these advantages, there is a large body of elution chromatographic data in the literature, and many descriptions of the instrumentation, experimental techniques, and theory.

On the other hand, the variation in thermodynamic properties as a function of concentration is also of vital interest, especially in the field of solution theory. Measurements of this type require a form of finite concentration chromatography called frontal chromatography. It is the purpose of this article to: (1) discuss the instrumental requirements for frontal chromatography as compared with those of elution chromatography, (2) describe the instrumentation and data logging system presently in use in our laboratory, and (3) give an illustrative example of the type and accuracy of data that can be obtained by frontal chromatography.

In the more difficult finite concentration form of chromatography, the sample must be introduced into the column at a constant, known mole fraction in the carrier gas. This can be done by continuous syringe injection or by using a precolumn saturator. In the latter case, the saturator must be 100% efficient over a wide temperature and flow-rate range.

The sample must enter the column in the form of a step function (concentration *vs.* time) and this is usually accomplished by a switching valve, either manual or pneumatic. This stream switching process must not cause a change in inlet pressure, or flow-rate and the valve itself must not distort the shape of the concentration profile.

The shape of the inlet concentration profile and the exact time the solute enters the column must be known. The usual practice is to place a detector at the inlet of the column as well as at the outlet. Also, the detector must be non-destructive and more critically, it must be linear (response *vs.* solute mole fraction) over a wide range of temperatures and flow-rates.

The flow-rate must be accurately monitored throughout the experiment and this is usually difficult because of the condensable component in the gas and the fact that the solute concentration, gas phase viscosity, and thermal conductivity all change with time during an experiment. The normal types of flowmeter such as soap film, capillary, rotameter, or mass flowmeter cannot be used under these conditions. Hence the flow-rate must be monitored by observing the retention distance of an unadsorbed solute in an empty column in a separate calibrated gas chromatograph placed at the analytical column outlet.

If these requirements are satisfied in the design of the instrumentation, the technique of frontal chromatography can be used to rapidly and accurately measure thermodynamic mixing data at finite concentrations. Elution methods can also be used for finite concentration data, however, several investigators[1-3] have reported that the elution data systematically deviate from static data for non-linear isotherms. In an excellent paper comparing elution and frontal techniques for isotherm measurement, Huber and Gerritse[4] showed that the frontal methods are superior to elution techniques for non-linear isotherms and less susceptible to experimental variables, such as column length, pressure drop, or flow-rate. In general, frontal chromatography is superior to elution or pulse chromatography for producing finite concentration activity coefficient data, partition and adsorption isotherms, and association constants. The advantages of finite concentration data, compared to infinite dilution data, make frontal chromatography an appealing technique in spite of the experimental difficulties.

THEORY OF FRONTAL CHROMATOGRAPHY

James and Phillips[5] were the first investigators to use frontal chromatography for non-analytical purposes, and the theory was further developed by Glueckauf[6,7]. Krige and Pretorius[8-11] have written papers on the theory of frontal chromatography and Conder and Purnell[12-15] published a series of papers, entitled "Gas Chromatography at Finite Concentrations", in which they discussed the theory of frontal chromatography and described the four basic techniques: (1) frontal analysis by characteristic point (FACP), (2) frontal analysis (FA), (3) elution on a plateau (EP), and (4) elution by characteristic point (ECP). The method used in our laboratory was developed by Glueckauf and is a modification of the FACP method 2 described by Conder and Purnell[14].

The basic procedure for obtaining partition isotherms from frontal analysis data is numerical integration[16] of eqn. 1.

$$Q = \frac{F_c{}^* P_0}{v_1 R T_c} \int_0^Y \frac{t_r - t_a}{1 - Y} \, \mathrm{d}Y \qquad (1)$$

Q is the amount of solute in moles per milliliter of solvent, $F_c{}^*$ is the outlet flow-rate upon switching the carrier gas stream, P_0 the atmospheric pressure, v_1 the liquid phase volume, R the gas constant, T_c the column temperature, Y the mole fraction of solute in the gas phase, t_a the retention time for air, and t_r the retention time at a particular increment of Y. The activity coefficient, $\gamma_2(T_c,0)$, is calculated from the partition isotherm by eqns. 2 and 3 according to Everett[17].

$$x_2 = \frac{(MW)(Q)}{(MW)(Q) + 1000\rho} \qquad (2)$$

$$\ln \gamma_2(T_c,0) = \ln \frac{Y_2 P_0}{x_2 P_2{}^0} - \frac{P_2{}^0}{RT_c}(B_{22} - v_2{}^0) + \frac{P_0 J_4^3}{RT_c}\{B_{22} - (1-Y)^2(B_{22} - 2B_{23} + B_{33}) - v_2{}^\infty\} \qquad (3)$$

x_2 is the mole fraction of solute in the liquid, MW the molecular weight of the liquid phase, ρ the density of the liquid phase, $P_2{}^0$ the vapor pressure of the solute at column temperature, B_{22} and B_{33} are the solute and carrier gas virial coefficients, respectively, and B_{23} the mixture virial coefficient calculated from the principle of corresponding states. The solute partial molar volume in solution at column temperature is given by $v_2{}^0$, $v_2{}^\infty$ is the solute partial molar volume at infinite dilution, and J_4^3 the compressibility factor.

EXPERIMENTAL

Chromatograph

The instrument modified for frontal chromatography was a Beckman GC-45 gas chromatograph (Beckman, Fullerton, Calif., U.S.A.). This instrument was chosen because of accurate column oven temperature control (±0.10°) and size of the column oven compartment. The instrument was equipped with a manual venting system which allowed ambient oven temperatures and a thermal conductivity detector. The space left by the manufacturer and intended to house a temperature programmer was found convenient for mounting flowmeter controls. Fig. 1 is a schematic diagram of the modified instrument.

Detector and columns

The flow path to the detector was altered so that the flow stream entering the head of the analytical column passed through one side of the detector and the outlet through the other side of the detector. In such an arrangement, a signal was observed when the composition of the gas entering the column was different from the composition at the column outlet. The reference column had no detectors and served only as a dynamic balance for the column head pressures and flow-rates. The column head pressures were monitored by means of conventional mercury manometers. A differential oil manometer was used to balance column head pressures. The columns were prepared from Chromosorb P-AW-DMCS, 60–80 mesh, support (Applied

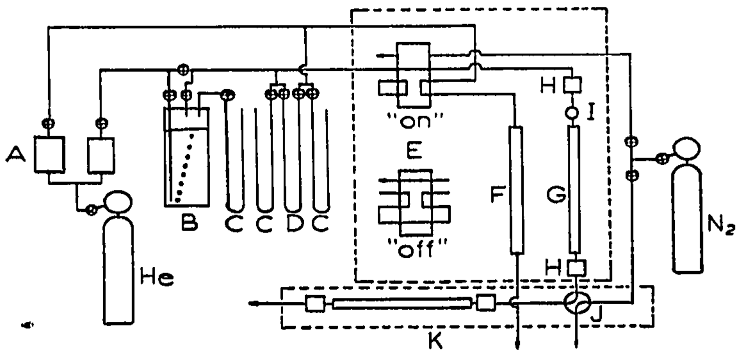


Fig. 1. Schematic diagram of chromatograph modified for frontal chromatography. A = Precision flow controllers; B = saturator; C = manometer; D = differential oil manometer; E = pneumatic gas switching valve; F = reference column; G = analytical column; H = thermal conductivity detector; I = injection port; J = gas sampling valve; K = flowmeter.

Science Labs., State College, Pa., U.S.A.) coated with 5.38% *n*-hexadecane (Applied Science Labs.). The solute was GC-spectrophotometric quality *n*-hexane (J. T. Baker, Phillipsburgh, N.J., U.S.A.).

Gas switching valve

A Beckman gas switching valve (Cat. No. 102 397) was installed directly in the detector oven. This provided rapid switching of column flow streams. In Fig. 1, the "on" position represents the flow stream configuration during which solute and carrier gas at a known mole fraction are introduced into the analytical column and the "off" position represents the flow stream configuration at which pure carrier gas is introduced into the analytical column.

Saturator

The saturator was constructed from 2 in. O.D. copper tubing and a 2 in. O.D. copper tee. The entire saturator and stainless-steel valves were immersed in a water-bath containing a 50:50 mixture by volume of ethylene glycol and water. The water-bath could be thermostated to ±0.50° and had a range of −10.0° to 110°. The carrier gas line leaving the saturator was heated with resistance heating wire at a temperature above saturator bath temperature.

The efficiency of the saturator was tested by measuring recorder response at several different flow-rates for a given saturator bath temperature (gas phase mole fraction). Table I shows the results of these tests at various flow-rates. The detector response was a linear function of gas phase mole fraction of the solute and the intercept was negligible except at the lowest flow-rates and no systematic deviation from linearity was observed at any of the flow-rates studied. The sensitivity of the thermal conductivity detector decreased slightly at the highest flow-rate but was effectively constant (±1%) in the range 30–90 ml/min.

Flowmeter

Calibration was accomplished by measuring the retention distance, D_R, for

TABLE I

LEAST SQUARES FIT OF DATA FOR RECORDER RESPONSE h AS A FUNCTION OF GAS PHASE MOLE FRACTION Y AT DIFFERENT FLOW-RATES

Flow-rate (ml/min)	*Slope* $\frac{\Delta h}{\Delta Y}$	*Intercept*	*Standard deviation*
30.0	192.8	4.54	0.23
50.0	193.1	0.93	0.39
70.0	188.9	−0.18	0.42
90.0	189.9	−1.14	0.25
110.0	178.9	−0.71	0.70

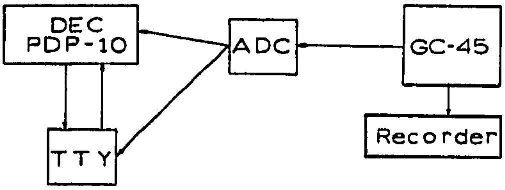
a nitrogen sample in pure carrier gas in an empty column at known corrected flow-rate measured by the usual soap film flowmeter. A plot of $1/D_R$ (cm^{-1}) against flow-rate (ml/min) was constructed and was used to determine flow-rates for solute+carrier gas mixtures.

Data logging system

The data logging system is shown in Fig. 2. The analog–digital converter (ADC) is a Beckman "Auto-Pro" Model 3111. The ADC supplied character data consisting of control characters for line feed, space, and carriage return, as well as two sample number decimal digits and four ADC output decimal digits for each reading in ACSII code. The device could be operated in a multiple sample mode allowing continuous sampling of chromatograph output over the desired counting interval. Intervals could be selected from 1 to 100 sec. During an experiment, the digitized ADC output was stored on magnetic disk directly "on line" to a PDP-10 computer (Digital Equipment Corporation, Maynard, Mass., U.S.A.) and echoed by the computer to the TTY set where it was also punched on paper tape for permanent record.

Example

Fig. 3 is a sample frontal chromatogram obtained from a frontal chromatography experiment with *n*-hexane in *n*-hexadecane at 30°. R is due to the detector response after switching solute+carrier gas to the inlet of the analytical column, S



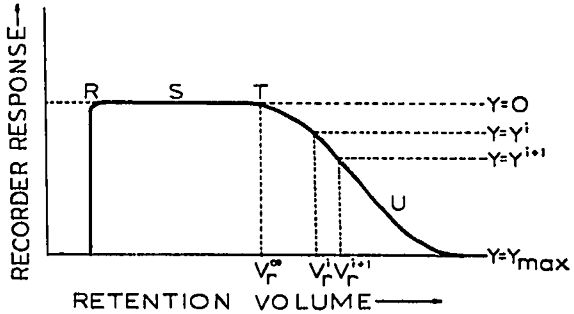


Fig. 2. Data logging system using the DEC PDP-10 computer.

Fig. 3. Typical frontalgram.

is the plateau during which saturation takes place, T is the breakthrough of the solute at the analytical column outlet corresponding to incomplete saturation, the sloping portion of the curve *U* represents an increasing retention volume with an increasing gas phase concentration of solute which is indicative of an anti-Langmuir type isotherm.

RESULTS AND DISCUSSION

Peterson and Helfferich[19] derived an equation for the retention volume of a solute at high concentrations in a solvent for which the partition isotherm is not linear.

$$V_r = V_m + (1 - Y)\left(\frac{\partial Q}{\partial C}\right)_c V_l \tag{4}$$

This is the generally accepted formula for obtaining partition isotherms from V_r data. However, in 1968 and 1969, Conder and Purnell[12-15] presented an alternative derivation and obtained a slightly different form of the equation.

$$V_r = V_m + (1 - J_3^2 Y)\left(\frac{\partial Q}{\partial C}\right)_{\bar{p}} V_l \tag{5}$$

where $(\partial Q/\partial C)_{\bar{p}}$ is the slope of the partition isotherm at the mean column pressure, $\bar{p}$, and J_3^2 is the James and Martin compressibility correction factor.

Due to experimental difficulties and a paucity of accurate experimental data obtained by non-chromatographic means, these two equations have not been compared at finite concentrations. The equations are identical at infinite dilution; however, there should be a systematic difference of high values of Y and $J_3^2 Y$. The accuracy of the isotherms obtained by frontal chromatography is dependent on the form of differential equation used, and a definitive test can be carried out by comparing the isotherms obtained by each equation with an accurate set of static data[20].

The test was carried out using the technique of measuring the retention volume of an elution sample on a partially saturated column. This mode of operation is usually called elution on a plateau, EP, and it is effected by saturating the liquid phase of hexadecane at a known value of Y, corresponding to completion of a regular frontal chromatography sorption experiment and then injecting a size gradient of *n*-hexane samples and extrapolating the observed retention distances to zero peak height. Corrected retention volumes were then calculated from the extrapolated retention distance according to established procedures for elution chromatography. The value of $(\partial Q/\partial C)_c$ was then calculated from eqns. 4 and 5.

Literature values for $(\partial Q/\partial C)_c$ were obtained by fitting the static data of McGlashan and Williamson[20] at 30 ° to an expression for an anti-Langmuir isotherm. Table II lists the experimental values calculated from eqns. 4 and 5. The agreement of static and chromatographic values of $(\partial Q/\partial C)_c$ is quite good over the range of gas phase mole fractions tested suggesting the validity of the general approach. However, data calculated in eqn. 4 without J_3^2 are slightly improved over eqn. 5 using J_3^2, suggesting that eqn. 5 may be more accurate. This is not a conclusive test, however, we have used eqn. 4 in our calculations rather than eqn. 5, for this reason.

TABLE II

COMPARISON OF LITERATURE VALUES OF $(\partial Q/\partial C)$ WITH EXPERIMENTAL VALUES CALCULATED FROM EQNS. 4 AND 5

γ	C *(mmoles/ml)*	$(\partial Q/\partial C)_c$ *(ref. 22)*	$(\partial Q/\partial C)_c$ *(eqn. 5)*	*% Development*	$(\partial Q/\partial C)_c$ *(eqn. 4)*	*% Development*
0.000	0.00	390	380	2.56	380	2.56
0.0272	1.22×10^{-3}	495	479	3.23	481	2.83
0.0492	2.19×10^{-3}	613	598	2.45	602	1.79
0.0963	4.33×10^{-3}	1087	1023	5.89	1034	4.88
0.1019	4.58×10^{-3}	1172	1147	2.13	1161	0.94
0.1260	5.65×10^{-3}	1708	1750	2.46	1770	3.62
				Av. 3.12		Av. 2.77

The excellent static data of McGlashan and Williamson provide a convenient test for experimental data from the system *n*-hexane in *n*-hexadecane as measured by frontal chromatography. Previous work has indicated that these data might be difficult to produce[16]. Problems which have been encountered are due to bleeding above 30° of columns coated with *n*-hexadecane, kinetic effects in the mass transfer of solute between gas and liquid phase causing non-equilibrium in the mixing of solute and solvent above certain flow-rates, and gross differences in the outlet flow-rate during an experiment observing the flow-rate used for calculation.

McGlashan and Williamson[20] fitted data of $\ln \gamma_2$ as a function of x_1 to an expression containing two adjustable parameters,

$$\ln \gamma_2 = \alpha x_1^2 + \beta x_1^2 (3 - 4x_1) \tag{6}$$

derived from Guggenheim's equation for the excess heat of mixing for simple mixtures. Employing a simple least squares curve fitting procedure on the best four of six data sets obtained by discarding the high and low data sets in Fig. 4, the values of α and β given in Table III were produced. Infinite dilution measurements gave a value of $\gamma_2^\infty = 0.905$ while the limiting form of eqn. 6 produced a value of $\gamma_2^\infty = 0.892$ for our values of α and β. Similar calculations for the static data of McGlashan and Williamson gave $\gamma_2^\infty = 0.897$.

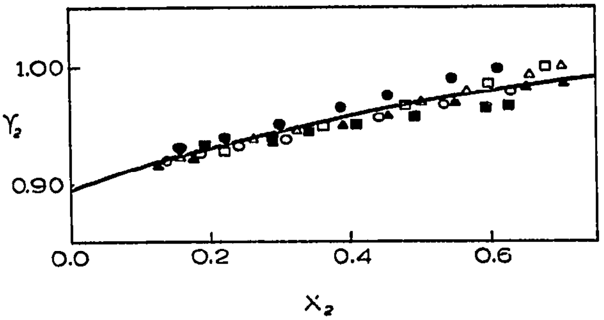


Fig. 4. Plot of the activity coefficient of *n*-hexane in *n*-hexadecane at 30° *vs.* the mole fraction of *n*-hexane in the solvent. ■ □ ● ○ ▲ △, this work (six experiments); ——, McGlashan and Williamson[20].

TABLE III

COMPARISON OF CALCULATED VALUES OF α AND β OBTAINED FROM A LEAST SQUARES FIT EQN. 6 FOR THE SYSTEM *n*-HEXANE IN *n*-HEXADECANE AT 30°

	α	β	*Standard deviation*
McGlashan and Williamson[20]	−0.1138	-6.022×10^{-3}	0.0147
This work	−0.1238	-9.823×10^{-3}	0.0237

Measurements of solute activity coefficients by frontal chromatography is inherently less accurate than static vapor pressure measurements, as the above results indicate. Nevertheless, the quite acceptable reproduction of the experimentally difficult system of *n*-hexane in *n*-hexadecane at 30° is quite encouraging. For many systems, applicable to frontal chromatography, sufficiently accurate data can be produced which are quite useful in deducing the nature of chemical interactions in non-electrolyte liquid mixtures with a considerable savings in experimental time and effort.

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