

MASTER

High-Precision Gas Chromatography*

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ABSTRACT

A high-precision chromatograph has been used for determination of differential thermodynamic quantities of two gas-liquid systems. Individual α values, and consequently $\Delta(\Delta H^\circ)$, were determined with a precision of $\pm 0.02\%$. The precision in the measurement of $\Delta(\Delta G^\circ)$ was $\pm 0.2\%$. These values represent an order of magnitude improvement over the best previously reported data. Heats of adsorption of hydrocarbons on carbon black and silica gel were also determined with a precision of $\pm 0.6\%$.

Gas chromatography has become a very useful technique for the study of the thermodynamics of closely related molecules. Rose, Stern, and Karger(1-3) have reported that, in gas-liquid chromatography, thermodynamically meaningful free-energy differences, for completely resolved components could be determined with a precision of ± 2 calories per mole. The uncertainty was attributed to the error of retention-time measurement.

Oberholtzer and Rogers (4) have reported a gas chromatographic system capable of precision in retention-time measurement better than $\pm 0.02\%$. Our goal was to use the high-precision instrument to study the differential thermodynamic parameters of some gas-liquid systems in order to determine the precision with which measurements could be made.

For measurement of the heat of adsorption, ΔH_a , at low surface coverages by static techniques, Beebe (5) reported errors of the order of ± 300 calories per mole or 7-8%. Therefore, we wished to investigate the applicability of the chromatograph to gas-solid systems with the hope that significant gains in precision might be achieved.

We also investigated the use of the high-precision instrument to obtain adsorption isotherms from the tail of a chromatographic peak (6).

EXPERIMENTAL

Apparatus. The chromatographic system has been discussed in detail (4). There were, however, some improvements made in the digital programmer (7). A new programmer has been constructed using Digital Equipment Corporation R and W series printed circuit cards. Noise rejection is complete, and changes in the logic design now allow more timing options. Digital data were recorded on punched paper tape and processed by a Hewlett-Packard 2116A computer. All experimental parameters were entered via a peripheral teletype.

Reagents. Two mixtures of structurally related compounds were prepared for the gas-liquid studies. The first mixture contained 51.0% 1-methyl-1-cyclohexene and 49.0% 3-methyl-1-cyclohexene (Aldrich Chemical Company, Inc.); the second mixture was 47.2% propyl acetate (Matheson, Coleman, and Bell) and 52.8% ethyl propionate (Eastman Organic Chemicals). The benzene, n-hexane, 1-hexene, n-heptane, and 1-heptene, used for the gas-solid studies, were of the highest obtainable purity.

Column Preparation. For the gas-liquid study, Sterling MT-FF Graphitized Carbon Black (Cabot Corporation) was pelletized, sieved to 60/80 mesh, and coated with sufficient Carbowax 400 (Varian Aerograph) to achieve a 4.5% by weight liquid load. A 610-cm X 0.32-cm i.d. stainless steel column was packed and conditioned for two hours at 100°C with a helium flow of 10 ml/min.

For the gas-solid studies two columns were used. The first was 50-cm X 0.32-cm i.d. packed with 0.374 g of 60/80 mesh Davidson No. 58 Silica Gel (Davidson Chemical), and the second was 15-cm X 0.32-cm i.d. packed with 0.210 g of 60/80 mesh Sterling MT-FF Graphitized Carbon Black.

Experimental Conditions. The two chemical mixtures used in the gas-liquid studies, 1- and 3-methyl-1-cyclohexene and propyl acetate-ethyl propionate, were chromatographed over the temperature ranges 78°-91° and 87°-97°C, respectively. Corrected retention times for the cyclohexene and ester systems ranged from about 450 seconds to 850 seconds and the differences from about 60 seconds to 150 seconds.

The temperature ranges for the gas-liquid systems and those used in the gas-solid studies are summarized in Table I. Adsorption isotherms for 1-hexene on silica gel were obtained over a temperature range of 65°-80°C. Flow rates in the gas-liquid studies were approximately 5 ml/min and in the gas-solid, 8 ml/min..

Calculations. Chromatographic peaks were detected using a Savitzky (8) smoothing routine associated with threshold

derivative peak-sensing as discussed previously (4).

The capacity ratio, \underline{k} , of each solute was calculated from

$$\underline{k} = \frac{\underline{t}_R - \underline{t}_m}{\underline{t}_m} \quad (1)$$

where \underline{t}_m and \underline{t}_R are the corrected retention times, at the peak mean, of a non-retained species (methane) and the solute, respectively.

The relative retention, α , of a two component mixture, was calculated from

$$\alpha = \frac{\underline{t}_{R2} - \underline{t}_m}{\underline{t}_{R1} - \underline{t}_m} = \frac{\underline{K}_2}{\underline{K}_1} \quad (2)$$

The relation for the standard molar free energy of solution is

$$\Delta G^{\circ} = -RT \ln \underline{K} \quad (3)$$

where \underline{R} is the gas constant, \underline{T} is the absolute temperature, and \underline{K} is the partition coefficient. Using equations 2-3 and the relationship,

$$\underline{K} = \frac{\underline{V}_g}{\underline{V}_l} \underline{k} \quad (4)$$

where \underline{V}_g and \underline{V}_l are the solute volumes in the gas and liquid phases respectively, it is easily shown that the difference in standard molar free energies of solution, $\Delta(\Delta G^{\circ})$, can be calculated from

$$\Delta(\Delta G^{\circ}) = -RT \ln \alpha \quad (5)$$

The standard molar heats of solution and adsorption, ΔH_s° and ΔH_a° , were obtained by a linear least-squares analysis of $\ln \underline{k}$ vs $1/\underline{T}$ from the relationship

$$\ln \underline{k} = - \frac{\Delta H^{\circ}}{RT} + \underline{C} \quad (6)$$

where \underline{C} is the constant of integration.

For comparison of precision, the differential enthalpies of reaction, $\Delta(\Delta H^{\circ})$, were calculated by two methods (see Table IV). Method I involved the measurement of \underline{k} for each substance and then determining the difference between the average ΔH° values calculated from equation 6. Method II involved the direct measure of α from each run and then determining the slope of a linear least-squares analysis of $\ln \alpha$ vs $1/\underline{T}$ using the expression

$$\ln \alpha = - \frac{\Delta(\Delta H^{\circ})}{RT} + \frac{\Delta(\Delta S^{\circ})}{R} \quad (7)$$

The standard molar differential entropies of reaction, $\Delta(\Delta S^{\circ})$, were calculated from the difference of intercepts in the plots of equation 6, from the intercept of the plot of equation 7, and from

$$\Delta(\Delta G^{\circ}) = \Delta(\Delta H^{\circ}) - T \Delta(\Delta S^{\circ}). \quad (8)$$

For determination of adsorption isotherms, the digitally recorded peak profiles were obtained, and the isotherms were calculated according to the procedure of Huber and Keulemans (6).

RESULTS

α Values. The α values for the separation of 1-methyl-1-cyclohexene and 3-methyl-1-cyclohexene are shown in Table II, along with the precision associated with each. In all cases, a minimum of five runs were made at each randomly selected temperature. Rose, Stern, and Karger (1) reported that they were able to measure α to $\pm 0.2\%$. This corresponded to a precision of ± 2 cal/mole in the calculation of $\Delta(\Delta G^{\circ})$ for the system they were studying. Table II shows that the precision in our worst case was $\pm 0.011\%$. This corresponded to a deviation in $\Delta(\Delta G^{\circ})$ of ± 0.2 cal/mole.

The entire experiment was repeated three months later (using the same column) with equal success in the precision of measurement of α . Upon comparison of the α values initially measured at any given temperature, the agreement was within 0.0005, with the later values always higher.

Table III demonstrates the effect of sample size on α . For a 1:1 mixture, the mean retention times were unaffected by a ten-fold change in sample size, and thus, α calculated from the peak mean, α_{mean} , was independent of sample size. Peak-maxima retention times decreased with increasing sample size, but the decrease was proportional, and α calculated from the peak maximum, α_{max} , was also independent of sample size. It is important to note that α_{mean} and α_{max} were significantly different.

Also shown in Table III are the effects of changes in the relative concentrations for a fixed total sample size. The α_{mean} showed no change over the 100-fold range of concentration ratios. In contrast, α_{max} showed a systematic increase with increase in the concentration ratio. This emphasizes the desirability of using peak means rather than peak maxima for retention measurements.

Differential Thermodynamic Quantities. The heats of solution, from equation 6, of 1-methyl-1-cyclohexene and 3-methyl-1-cyclohexene were -7236 ± 6 and -6971 ± 8 calories per mole, respectively. Table IV shows a comparison of the differential thermodynamic quantities calculated by the difference approach, method I, and the direct approach, method II.

By the difference approach, $\Delta(\Delta H^\circ)$ was -265 ± 10 cal/mole. This resulted in a $\Delta(\Delta S^\circ)$ of -0.35 ± 0.03 e.u., when calculated from equation 8. By contrast, when $\Delta(\Delta S^\circ)$ was calculated from the difference of the intercepts of the plots of equation 6, a value of -0.33 ± 0.15 e.u. was determined. The large standard deviation was expected since the data were extrapolated more than 50-times their total range to obtain the intercept. The agreement of $\Delta(\Delta S^\circ)$, calculated by both techniques, is indicative of the high precision of the chromatograph.

Using the same raw data, $\Delta(\Delta H^\circ)$ was determined by the direct approach. This gave a value of -266.85 ± 0.02 cal/mole. The 500-fold improvement in precision reflects the added power of the direct measurement. Calculation of $\Delta(\Delta S^\circ)$, from equation 8, resulted in a value of -0.350 ± 0.001 e.u. One sees a 30-fold improvement in the precision of $\Delta(\Delta S^\circ)$ when comparing the direct with the difference approach. The $\Delta(\Delta S^\circ)$, found from the intercept of equation 7, was in good agreement with those values described above.

In an effort to determine whether or not the high precision was unique to the hydrocarbon mixture, similar studies were made on a mixture of ethyl propionate and propyl acetate. The precision of measurement of the individual α values was as good or better than that reported for the methylcyclohexenes. As can be seen in Table IV, the precision of measurement of the differential thermodynamic quantities was comparable to that for the first hydrocarbon mixture and, hence, it should be typical of what one might reasonably expect for many gas-liquid systems.

Gas-solid Systems. Table V shows the ΔH_a values for five adsorbates on carbon black and silica gel. The retention time showed no sample size dependence on carbon black; therefore, a simple arithmetic average of 3-5 retention times at each temperature was used. For the wide-pore silica gel, an approximation of the sample size- retention time dependence was obtained using a quadratic least-squares fit of concentration vs. retention. Five concentrations ranging from 1 ppt to 100 ppm were used. A standard sample size, intermediate in value, was then selected and the corresponding retention time was used in calculation of the thermodynamic parameters.

The carbon black system gave a precision of better than ± 60 cal/mole for ΔH_a . For the silica gel, the relatively non-polar 1-hexene yielded results of almost comparable precision, but the more polarizable benzene, which exhibited badly tailed peaks, gave deviations of the range of ± 300 cal/mole. Thus, the precision in gas-solid chromatography was inferior to that obtained in the gas-liquid work, and was very dependent on the system studied.

Adsorption Isotherms. Adsorption isotherms were determined from the tails of chromatographic peaks in the manner described by Huber and Keulemans (6). For the purpose of this study, neither the silica gel surface area nor the absolute detector response were determined. Consequently, surface coverage is tabulated in units of microcoulombs per gram of adsorbent.

Table VI shows the reproducibility of partial pressures at given surface coverages for 1-hexene on a wide pore silica. The isotherms were reproducible to $\pm 2\%$ regardless of flow rate.

Heats of adsorption determined from isotherms at several temperatures, showed standard deviations of from $\pm 2\%$ at high relative surface coverages to $\pm 8\%$ at the lowest values. The absolute value of ΔH_a^0 , about 12.8 kcal/mole, was also dependent upon the programming algorithm used for baseline determination in the peak sensing program. Naturally, this effect was more pronounced at lower surface coverages, where the problems of detecting the end of the peak with derivative peak-sensing were more critical.

For example, at relative surface coverage of 6×10^{-4} $\mu\text{coul/g}$, ΔH_a values calculated from separate runs agreed only within 8%, while at a relative coverage of 1×10^{-2} $\mu\text{coul/g}$, the agreement was 1%.

DISCUSSION

In the two gas-liquid systems studied, α , and consequently $\Delta(\Delta H^\circ)$, were determined with a precision of $\pm 0.02\%$. In the methylcyclohexene system a plot of α vs. T showed a distinct change in slope below 81°C . This was probably the result of another mechanism, such as adsorption, coming into play. The fact that the change could be detected, with certainty, over a range of only three degrees ($78^\circ\text{-}81^\circ\text{C}$) emphasizes the sensitivity and reliability of the overall chromatographic system. In any case, the thermodynamic quantities reported earlier were calculated only from the chromatographic data above 81°C .

Karger (2) has pointed out that one must determine α for severely overlapped peaks using separate runs for each component. When that was done for 1- and 3-methyl-1-cyclohexene, the α values had a standard deviation of $\pm 0.06\%$ compared to $\pm 0.02\%$ for the mixtures. (The greater uncertainty may have been due to the longer period of time required to obtain the data in the former case, but it is still quite satisfactory.) for modest amounts of overlap one should be able to use mixtures for determining α by employing peak maxima rather than peak means. In spite of the difference in the absolute values for α determined by each method (Table III), useful estimates of $\Delta(\Delta G^\circ)$ should still be obtainable from mixtures which are incompletely resolved. The data would be much faster to obtain and might still be sufficiently precise compared to that from runs on single components. Furthermore, it is important to note that, for our system where peak tailing was minimal, the differential heats of solution obtained from α_{max} and α_{mean} were not significantly different (266.80 and 266.85 cal/mole, respectively). Of course, such agreement would not be expected to hold universally but would be a function of the difference in the changes in the two peak shapes with temperature.

In some of the initial runs, several large leaks were detected in the gas lines. The standard deviations in α were of the order of ± 0.0003 , only a factor of two larger than those reported above, but the average value of α was unaffected. Thus, $\Delta(\Delta G^\circ)$ and $\Delta(\Delta H^\circ)$ could still be determined accurately and with good precision. The reproducibility of k , however, was very much affected by the leaking system. Differential heats of solution, calculated by the difference method, showed standard deviations of about ± 300 cal/mole.

For the measurement of ΔH_a in the gas-solid systems, the limiting factor in the precision appears to be the nature of the system studied. Reasons for this include not only the large sample-size dependence found for the capacity ratio with most gas-solid systems, but also adsorbent inhomogeneity. Even for the "homogeneous" graphitized carbon black, the results were inferior to those for the gas-liquid systems.

Heats of adsorption, for 1-hexene on silica gel, determined from the isotherms (12.8 kcal/mole) were not in good agreement with those determined for the same adsorbent-adsorbate system using the peak method, equation 6 (10.5 kcal/mole). There are several possible explanations for this discrepancy. The experimental procedure was not optimized for either case. The isotherm method required a badly tailed peak and a sharp leading edge, while the peak method assumes a symmetrical peak. In order to meet both sets of conditions, it became necessary to run the two experiments at very different temperature ranges; 70° - 83°C for the isotherm method and 120° - 135°C for the peak method. Even then, neither set of peak-shape requirements were met in full, and the calculations had to be made on data that were less than ideal. For the isotherm method, the back of the peak was not badly tailed and the leading edge showed effects of diffusional broadening. Furthermore, for the peak method, it was not possible to completely eliminate tailing by going to the higher temperature range. A better choice of a gas-solid system which more closely meets both sets of requirements over a limited temperature range should facilitate comparison of the two methods.

The critical contributions of digital control and digital data acquisition cannot be emphasized enough. These techniques were

absolutely necessary in order to obtain data with the reported precision. The stability and precision that have been demonstrated by this instrument should allow it to be applied to the study of systems which exhibit very subtle changes in their chromatographic behavior. Examples of these might include such compounds as diastereoisomers and enantiomers, or isotopically substituted species.

The fact the differences in k and ΔH for two isomers have been measured differentially with high precision indicates that Kovats Indices and their temperature coefficients should be susceptible to similar improvement. However, it is important to realize that the chemistry of the system may frequently limit the precision and accuracy of the experimental results for gas-liquid systems just as we have found for the gas-solid systems. Furthermore, there is always the basic question of how accurately a non-equilibrium system like gas chromatography can describe an equilibrium process. Use of equipment such as that employed in the present study will now permit those questions to be answered.

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Table I. Experimental Temperature Ranges
for Compounds Studied

Mixtures and compounds studied	Column temperature range, °C		
	Carbowax 400 on carbon black	Carbon black	Silica gel
Methylcyclohexene mixture	78-91	-	-
Ester mixture	87-97	-	-
n-Hexane	-	130-157	-
n-Heptane	-	130-157	-
1-Heptene	-	130-157	-
1-Hexene	-	72-88	120-135
Benzene	-	-	134-150

Table II. α and $\Delta(\Delta G^\circ)$ as a function of Temperature,
 For the Separation of 1-Methyl-1-Cyclohexene
 and 3-Methyl-1-Cyclohexene on Carbowax 400

$t, ^\circ\text{C}$	α^a	$\Delta(\Delta G^\circ)$
78.35	1.2297 ± 0.00009^b	144.44
80.30	1.2276 ± 0.00011	144.02
80.56	1.2268 ± 0.00007	143.67
81.68	1.2244 ± 0.00010	142.74
81.98	1.2241 ± 0.00005	142.68
84.61	1.2211 ± 0.00008	142.00
86.12	1.2189 ± 0.00013	141.31
87.18	1.2177 ± 0.00001	141.02
89.80	1.2137 ± 0.00010	140.68
90.38	1.2133 ± 0.00009	139.66

^a a minimum of five determinations of α at each temperature

^b standard deviation for the individual results

Table III. Effects of Concentration on α
 For the Separation of 1-Methyl-1-Cyclohexene
 and 3-Methyl-1-Cyclohexene

A. Effect of sample size on 1:1 mixture at 83.32 °C

Relative sample size	α	
	Peak means	Peak maxima
1 ^a	1.2226 ± 0.00010	1.2241 ± 0.00011
5	1.2226 ± 0.00008	1.2240 ± 0.00009
10	1.2227 ± 0.00009	1.2240 ± 0.00010

B. Effect of changes in the concentration ratio
 of each component^a at 84.61 °C

<u>3-methyl-1-cyclohexene</u> <u>1-methyl-1-cyclohexene</u>	α	
	Peak mean	Peak maxima
1:10	1.2211 ± 0.00011	1.2219 ± 0.00013
1:1	1.2211 ± 0.00005	1.2223 ± 0.00009
10:1	1.2211 ± 0.00007	1.2225 ± 0.00011

^a detector uncalibrated ; sample sizes are relative

Table IV. Differential Thermodynamic Quantities Calculated
From Gas Chromatographic Data

A. Methylcyclohexenes (84.61 °C)

Difference				Direct		
$\Delta(\Delta\dot{H})$	$\Delta(\Delta\dot{S})^a$	$\Delta(\Delta\dot{S})^b$	$\Delta(\Delta\dot{G})^c$	$\Delta(\Delta\dot{H})$	$\Delta(\Delta\dot{S})^a$	$\Delta(\Delta\dot{S})^d$
-265 ± 10	-0.35 ± 0.03	-0.33 ± 0.15	-142.00 ± 0.2	-266.85 ± 0.02	-0.350 ± 0.001	-0.35 ± 0.11

B. Ethyl propionate - propyl acetate (90.13 °C)

-117 ± 11	-0.11 ± 0.03	-0.11 ± 0.09	-77.5 ± 0.2	-115.98 ± 0.02	-0.110 ± 0.002	-0.11 ± 0.06
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^a from equation 8

^b from difference in intercepts of $\ln k$ vs. $1/T$

^c from equation 5

^d from intercept of $\ln \alpha$ vs. $1/T$

Table V. $\Delta\bar{H}_a$ For Adsorbates on Silica Gel
and on Graphitized Carbon Black

<u>Adsorbate</u>	$\Delta\bar{H}_a$, kcal/mole	
	<u>Silica gel</u>	<u>Carbon black</u>
n-Hexane	-	9.56 \pm 0.05
n-Heptane	-	11.16 \pm 0.04
1-Heptane	-	10.69 \pm 0.03
1-Hexene	10.47 \pm 0.06	9.34 \pm 0.02
Benzene	10.8 \pm 0.3	-