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FRANK J. SEILER RESEARCH LABORATORY

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THEORETICAL MODELING OF SCOT COLUMNS

Robert H. Fogelsong

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This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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A description of the thermodynamic processes that occur within a SCOT column is presented. The unique geometry of the SCOT column was found to slightly alter the mathematical description of the thermodynamic phenomena as compared to the traditional packed column. The correlation derived from this thermodynamic description was used to determine experimental values for the heats of vaporization and boiling points for several light alcohols to verify its usefullness and validity.

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SUMMARY

The use of thermodynamics and physical chemistry as applicable to SCOT column phenomenon is applied as a modeling technique to derive a correlation suitable for calculation of heats of vaporization and boiling points for SCOT column geometry. Beginning with the expression for partial pressure as given in terms of activity coefficients, mole fraction in a solution and vapor pressure of the solute, and then applying various algebraic substitutions, correlating several chromatographic expressions and incorporating SCOT column peculiarities, an expression has been derived that permits the easy calculation of heats of vaporization and boiling points. The mathematical derivation closely parallels the theory associated with packed chromatographic columns, yet incorporates discussions and physical application of factors particular to SCOT columns to modify/confirm the usefulness of packed column theory for SCOT column applications. Experimental work as derived from a SCOT column in a Perkin-Elmer chromatograph is supplied to permit utilization of said correlation and to verify its validity.

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INTRODUCTION

The use of column chromatography as as analytical tool has increased at a significant rate and has resulted in many practical applications throughout industry. Many examples of appropriate applications include the use of gas-liquid chromatography for the determination of transport and/or thermodynamic properties, the use of chromatography for the purification of small commercial quantities of speciality chemicals, and the use of gas chromatography as the primary analytical device for direct measurement and control of continuous processes.

Thus, the ever-increasing need for better column performance has brought about the introduction of a new concept in gas-liquid chromatographic columns. The support coated open tubular column (SCOT) has presented researchers and practical applications experts with a tool that combines the advantages of the traditional packed column and those of the open tubular design. Advantages gained through reductions in analysis times and significantly smaller pressure drops have increased the popularity of the SCOT column. Better separation capabilities and larger sample sizes associated with the SCOT column have permitted many practical applications not previously possible.

As was characteristic of a young idea in science, the theoretical study and analysis of this analytical tool lagged practical applications of the SCOT column. Numerous papers are available directly related to practical applications of SCOT geometry. Theoretical studies are limited but becoming more available. The SCOT column itself has been partially responsible for this limited amount of published theory. The complex mathematical description of the support layer adhering to the column wall has not lent itself to easy solution. Thus, one of the goals of this work will be to apply some basic thermodynamic principles as applicable to packed column geometry and to modify the results in order to obtain a suitable description of parallel thermodynamic occurrences within SCOT columns. This particular application will result in the use of said thermodynamic theory to derive the physical properties (T_b and ΔH_v) of several simple alcohols as a verification of the applicability of the theory ulitized to describe intercolumn phenomenon.

To achieve different results, numerous researchers have applied the use of modeling and thermodynamic theory with packed columns. As examples, the use of gas-liquid chromatography was used by Hoare and Purnell (1,2) to evaluate vapor pressure, boiling points, latent heats and entropies of solution. Their work closely parallels the thermodynamic applications to be presented in this article. Littlewood, et al. (3) measured heats of solution from chromatographic data. The calculation of dispersion coefficients by means of moments has been done by Horn (4), while Giddings, et al. (5) determined values for gaseous diffusion coefficients by using theoretical correlations based on chromatographic theory.

THERMODYNAMIC DERIVATION

As has been commonly done in past thermodynamic modeling of packed column geometry, it will be assumed that the partial pressure of the solute over the solution within a SCOT column can be described by the following equation:

$$p = p^{o} \gamma x \tag{1}$$

where p is the partial pressure of the solute over the solution, γ is the activity coefficient, x is the mole fraction in solution and p^{o} is the vapor pressure of the solute. The partial pressure of the solute over the solution can also be expressed as follows:

$$p = C_{g}^{s} R T \tag{2}$$

where C_{g}^{s} is the molar concentration of the solute in the gas phase. The mole fraction in the solution can be represented by the following equation:

$$x = N_{1}^{s} / N_{1} + N_{1}^{s} \approx N_{1}^{s} / N_{1} \tag{3}$$

where N_{1}^{s} is the number of moles of solute in solution in N_{1} moles of solvent. Since N_{1} is equal to the volume of solvent (V_{1}) divided by the molar volume (V_{1}^{m}), the following expression can be algebraically derived from equation (3):

$$x = N_{1}^{s} V_{1}^{m} / V_{1} = C_{1}^{s} V_{1}^{m} \tag{4}$$

Substituting equations (2) and (4) into equation (1) yields the following:

$$C_{1}^{s} / C_{g}^{s} = K = R T / V_{1}^{m} \gamma p^{o} \tag{5}$$

where K is the familiar partition coefficient. Then, by definition,

$$V_{R} = K V_{1} \tag{6}$$

where V_{R} is the net retention volume. Therefore,

$$V_{R} = (R T / \gamma p^{o})(V_{1} / V_{1}^{m}) = (R T / \gamma p^{o})(w / M_{1}) \tag{7}$$

where w is the grams of solute and M_{1} is the molecular weight of the solute. Therefore the retention volume/gram weight of solute is

$$V_{R}^{T} = R T / \gamma p^{o} M_{1} \tag{8}$$

The specific retention volume is also defined by Ambrose, et al. (6) as

$$V_{g} = 273 V_{R}^{T} / T \tag{9}$$

Therefore,

$$V_g = (273\ R) / (\gamma\, p^o\, M_1) \qquad (10)$$

or

$$V_g = 1.7 \times 10^7 / \gamma\, p^o\, M_1 \qquad (11)$$

where $\gamma = \gamma_a\, \gamma_t$. As another thermodynamic principle is applied, at equilibrium,

$$dG_{vap} = dG_{liq} \qquad (12)$$

where G is Gibbs free energy, and

$$dG = v\ dp - s\ dT \qquad (13)$$

where v is the volume per mole of pure substance and s is the entropy per mole of pure substance. Therefore, from equations (12) and (13),

$$dp / dT = (S_1 - S_v)/(V_1 - V_v) \qquad (14)$$

but,

$$\Delta S = \Delta H_v / T \qquad (16)$$

where ΔH_v is the heat of vaporization of the solute. Therefore,

$$dp / dT\ (V_1 - V_v) = \Delta H_v / T \qquad (16)$$

From general chromatographic theory the following correlation can be derived:

$$V_1 - V_v = V_1 (1 - \beta) = (R\ T / p)(1 / \beta - 1) \qquad (17)$$

where β is the total volume of gas in a column divided by the total volume of liquid in a column. This correlation will thus allow for the unique geometry of the SCOT column as will later be discussed. Therefore,

$$dp / dT\ (R\ T / p)(1 / \beta - 1) = \Delta H_v / T \qquad (18)$$

or

$$d\ \ln p / dT = (\Delta H_v / R\ T^2)(\beta / 1 - \beta) \qquad (19)$$

if $\Delta H_v \neq f(T)$,

$$p^o = \exp\ (\Delta H_v / R\ T\ (\beta / \beta - 1) + 2.3\ C) \qquad (20)$$

Referring back to equation (11), it now becomes necessary to develop an expression for γ_T. Khan (7) has verified the following expression for γ_T:

$$\ln \gamma_T = \Delta H_M / R T \qquad (21)$$

where ΔH_M is the heat of mixing. Therefore, combining equations (20) and (21) results in the following relationship:

$$\gamma_T p^o = (p^o)^a \exp (2.3 C (1 - a)) \qquad (22)$$

where

$$a = (\Delta H_M + \Delta H_v (\beta / \beta - 1)) / \Delta H_v$$

a = constant for an ideal solution

Substitution of equation (22) into equation (11) yields the following:

$$V_g = \frac{1.7 \times 10^7}{\gamma_a M_l (p^o)^a \exp (2.3 C (1 - a))} \qquad (23)$$

or

$$\log V_g = - A \log p^o + C$$

Therefore, by using previous definitions for p^o,

$$\log V_g = A' (\Delta H_v / R T)(\beta / \beta - 1) + D \qquad (24)$$

An expression similar to equation (24) has been derived for packed columns (1,2) and used to calculate ΔH_v with reasonable success. The above relationship was derived by using the same thermodynamic relationships as has been applied by previous researchers. The inclusion of the β term as it applies to SCOT column geometry modified a portion of the packed column derivation. This modification was significant and proved to provide an additional term as the derivation proceeded. The final result would thus indicate SCOT columns can be used in exactly the same way as packed columns to obtain experimental values of ΔH_v and T_b (boiling point) via the following expression:

$$\Delta H_v / T_b = \text{constant (Trouton)} \qquad (25)$$

RESULTS

The experimental results necessary to verify the usefulness of equation (24) was obtained from a Perkin-Elmer Model 990 Gas Chromatograph. The actual separation device was a fifty foot, .020 inch diameter SCOT column containing a Carbowax 1540 liquid phase. A β factor of fifty was used to characterize this column. Various physical modifications were incorporated to allow those measurements necessary to supply data permitting the calculation of the partition coefficient (K). Ethanol and isopropyl alcohol were used as liquid samples. Temperature was varied, permitting the determination of K , and consequently V_g , over a fairly significant temperature range. A plot of log V_g versus 1/T was constructed. The resulting slope must be equal to the following expression:

$$\text{Slope} = (\beta / \beta - 1)(\Delta H_v / R)$$

The results of the mathematical determination of both ΔH_v and T_b are presented in Table 1 . Comparative values of both parameters are presented as obtained from Perry's Chemical Engineer's Handbook (8).

TABLE 1

COMPARATIVE VALUES OF H_v AND T_b

Parameter	Ethanol	Isopropyl Alcohol
T_b (this work-K^o)	345	356
T_b (Perry's-K^o)	351	365
ΔH_v (this work-cal/m)	9240	9520
ΔH_v (Perry's-cal/m)	9304	9550

CONCLUSIONS

The applicability of many of the same thermodynamic relationships for packed chromatographic columns to SCOT column geometry is apparent. By thermodynamically modeling a SCOT column in much the same manner as has been accomplished for packed columns and incorporating an appropriate modification to account for the extreme ratio of V_g / V_l in a SCOT column as opposed to a packed column, it was determined that the incorporation of said modification would slightly modify the final thermodynamic relationship. This final relationship was similar to that obtained for a packed column. The usefulness and validity of the SCOT column geometry associated relationship has been demonstrated by the fairly accurate results obtained by combining said relationship with experimental results obtained from the labratory.

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NOMENCLATURE

a	$(\Delta H_M + \Delta H_v \ (\beta / \beta - 1)/\Delta H_v$
A	Constant
C	Integration Constant
C_g^s	Concentration of solute in gaseous phase
C_1^s	Concentration of solute in solvent
D	Integration Constant
G	Gibbs Free Energy
ΔH_M	Heat of Mixing
ΔH_v	Heat of Vaporization
K	Partition Coefficient
M_1	Molecular Weight of Solvent
N_1	Moles of Solvent
N_1^s	Moles of Solute in Solution
p	Partial Pressure
p^o	Vapor Pressure
R	Gas Constant per Mole
s	Entropy per Mole of Pure Substance
ΔS	Entropy of System
T	Temperature
T_b	Normal Boiling Point
v	Volume per Mole of Pure Substance
V_g	Specific Retention Volume
V_1	Volume of the Liquid Phase
V_1^m	Molar Volume

V_R^T	Retention Volume/Gram Weight of Solvent
V_R	Net Retention Volume
V_v	Volume of Gaseous Phase
w	Grams of Solvent
x	Mole Fraction in Solution
β	Beta Factor
γ	Activity Coefficient
γ_a	Concentration Dependent Activity Coefficient
γ_T	Temperature Dependent Activity Coefficient


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