Physicochemical Applications of Gas Chromatography

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To

MARIE and MARY

and

HOWARD PURNELL

from whom we have both learned
most of what we know about
gas chromatography

Preface

Since its inception in 1952 gas chromatography (GC) has enjoyed an explosive growth throughout the world and is now a well-known technique in all disciplines of chemistry. The reasons for its proliferation are undoubtedly many, but, chiefly, gas chromatography is an extremely powerful as well as sensitive separations method which certainly has other uses that are of compelling interest in many disciplines. These *physicochemical* (nonanalytical) applications, which are the subject of this book, require some exposition of the background physical chemistry which, however, should not be construed as irrelevant to the interests of analytical chemists. On the contrary, the topics covered here should be of value to all practicing chromatographers who wish to know more than how to inject a sample and record the results on a strip chart.

Because we hope to encourage newcomers to the field, we have tried to present the material, insofar as possible, in a "user-oriented" fashion. However, as the subject continues to expand, we must, inevitably, be found guilty of omissions. Indeed, the development of physicochemical uses of GC appears to be limited only by the number of research groups in the field and the time devoted to it; our purpose in producing this book will have been fulfilled if we stimulate or otherwise encourage new developments by workers in this area.

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R.J.L.
R.L.P.

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PART IV PROPERTIES OF PURE SUBSTANCES

Symbols

Symbol	Definition	Page No.
a_i	Solute activity in *i*th phase; activity of species *i*	14
A	Column cross-sectional area	17
A	Eddy diffusion term in van Deemter equation	21
A_{DA}	UV charge-transfer complex absorbance	156
A_L	Liquid-phase surface area	31
A_S	Adsorbent surface area	19
A_S	Measure of peak asymmetry	28
b	Carrier fugacity coefficient divided by RT	90
B	Baseline distance from perpendicular through peak maximum to tangent to rear side of peak	28
B_o	Longitudinal diffusion term in van Deemter equation corrected to 1 atm	21
B_{11}	Solute virial coefficient	24
B_{12}	Solute-carrier virial coefficient	24
B_{22}^c	Carrier virial coefficient at column temperature	62
c	Solute concentration in mobile phase	24
c	Fraction of solute complexed in stationary phase	160
c	BET equation constant	220
C_{A}	Additive concentration in (binary) stationary phase	158
C_{D}	Donor solute concentration in (binary) stationary phase	158
C_{D}^0	Donor solute concentration in pure stationary phase	158
C_{D}^M	Donor solute concentration in mobile phase	158
C_{DA}	Complex concentration in stationary phase	158
C_L	Solute concentration in stationary phase	14
C_L	Stationary phase mass transfer non-equilibrium term in van Deemter equation	21
C_M	Solute concentration in mobile phase	14
C_M^o	Mobile-phase mass transfer non-equilibrium term in van Deemter equation corrected to 1 atm pressure	21

C_p	Solute heat capacity	124
C_p^e	Solute excess heat capacity	117
d_f	Average stationary-phase film thickness	22
d_p	Packing particle diameter	22
D_{12}^o	Solute-carrier interdiffusion coefficient at 1 atm pressure	22
D_{13}	Solute-stationary phase interdiffusion coefficient	22
D_{eff}	Taylor diffusion coefficient	254
$\Delta\bar{E}_v$	Molar internal energy of vaporization	120
f	Cross-sectional column flow rate	89
f_i	Fugacity of species i	83
F	Uncorrected volume flow rate at column outlet	16
F	Stationary-phase surface area enhancement term in Golay equation	22
F	Baseline distance from perpendicular through peak maximum to tangent to front side of peak	28
$F(o)$	Flow rate of mobile phase at column outlet in FAGC	25
F_c	Corrected volume flow rate at column outlet	16
F_c'	Corrected volume flow rate at column inlet	62
F_i	Uncorrected volume flow rate at column inlet	62
F_o	Uncorrected volume flow rate at column outlet	62
$\Delta\bar{G}_s$	Molar Gibbs free energy of solution	112
h	Reduced plate height	22
h	Plateau height in FAGC expression for V_R^0	28
h_M	Peak maximum detector signal	53
H, $HETP$	Height equivalent to a theoretical plate	4
ΔH_a^0	Solute heat of adsorption at zero surface coverage	216
ΔH_a^s	Solute isosteric heat of adsorption	216
$\Delta\bar{H}^e$	Solute excess molar enthalpy of mixing	116
$\Delta\bar{H}_s$	Solute molar heat of solution	111
$\Delta\bar{H}_v$	Solute molar heat of vaporization	111
i	Detector signal noise level	53
I^d	Ionization potential	102
I_i	Kovats retention index of solute i	93
j	James-Martin carrier compressibility correction factor	18
j'	Carrier compressibility correction factor for calculation of average flow rate from that at column inlet	62
J_n^m	Generalized carrier compressibility correction factor	18
k	Inverse of k'	20
k	Boltzmann's constant	122
k	Rate constant	237

k'	Solute capacity factor	20
K	Packed-column specific permeability coefficient	17
K'	Defined form of equilibrium constant	160
K_1	Complex stability constant	153
K_a	Lewis relative acidity constant	139
K_{eq}	Thermodynamic equilibrium constant	160
K_R	Solute liquid/gas partition coefficient	14
$K^0_{R(i)}$	Solute partition coefficient with pure stationary phase *i*	159
K_S	Solute liquid/gas interfacial adsorption partition coefficient	31
l	Cell path length	156
l_A	Chart distance from point of injection to air peak maximum	48
l_R	Chart distance from point of injection to solute peak maximum	48
L	Column length	4
MW_L	Stationary-phase molecular weight	20
n	Number of carbon atoms	85
n_L	Mole number of stationary phase	20
n_1^L	Solute mole number in stationary phase	20
n_1^M	Solute mole number in mobile phase	20
N	Number of theoretical plates	4
p	Pressure	17
$\bar{p}$	Average column pressure	17
p_1^0	Solute bulk vapor pressure	19
p_{fm}	Pressure at flowmeter exit	16
p_i	Column inlet pressure	18
p_o	Column outlet pressure	17
p_w	Water-vapor pressure at flowmeter temperature	16
q	Solute concentration in stationary phase	24
r	Column tube radius	22
r	Chart speed	48
r	Ratio of solvent: solute molar volumes	119
R	Gas constant	14
R	Retention ratio	23
s	Chart speed	25
S	Adsorbent specific surface area	19
$\Delta\bar{S}_s$	Molar entropy of solution	112
t	Student factor	54
t_0	Time at which mobile phase is changed from pure carrier to solute plus carrier in FAGC	24

t_1	Solute break-through time in FAGC	24
t_2	Time at which mobile phase is changed from solute plus carrier to pure carrier in FAGC	24
t_A	Dead (air) time	16
t_R	Solute raw retention time	15
t'_R	Adjusted retention time	19
T	Column temperature	14
T^c	Critical temperature	84
T_{fm}	Flowmeter temperature	16
u	Linear velocity of carrier	7
$\bar{u}$	Average linear velocity of carrier	15
u_o	Linear velocity of carrier at column outlet	17
v_1^0	Solute bulk molar volume	85
v_1^∞	Solute molar volume at infinite dilution in stationary phase	89
v_L	Stationary-phase area in a thin segment of column	89
v_M	Mobile-phase area in a thin segment of column	89
V	Volume of sorbate	220
V_A	Dead (air) volume	18
V^c	Critical volume	84
V_g^0	Solute specific retention volume corrected to 0 °C	19
V_g^T	Solute specific retention volume at column temperature	19
V_L	Volume of stationary phase	15
$\bar{V}_L$	Stationary-phase molar volume	20
V_M	Volume of mobile phase	15
V_M	Corrected dead volume	18
V_M	Sorbate monolayer volume	220
V_N	Solute net retention volume	18
V_R	Solute raw retention volume	16
V'_R	Solute adjusted retention volume	16
V_R^0	Solute corrected retention volume	18
$w_{\frac{1}{2}}$	Peak width at half-height	28
w_b	Baseline distance between peak front and rear tangents	28
w_L	Weight of liquid phase	19
w_S	Weight of adsorbent phase	19
x_1^L	Solute mole fraction in stationary phase	19
y	Solute mole fraction in mobile phase	24
z	Solute carbon number for *n*-alkanes	93
α	Relative retention ratio	20
β	Phase ratio	20

β	Virial parameter in expression for pressure-dependence of V_N	30
β'	Virial parameter corrected for carrier solubility effects	91
β_L	Stationary-phase mass transfer non-equilibrium term in Giddings equation	22
γ	Tortuosity factor in van Deemter equation	21
γ_1^∞	Fully-corrected solute activity coefficient	30
γ_p^∞	Uncorrected solute activity coefficient	19
δ	Solubility parameter	120
δ	NMR shift	156
Δ	NMR shift difference due to complex formation	156
ε	Packed-column porosity	17
$\varepsilon_{\mathrm{DA}}$	Molar absorptivity of complex DA	156
ζ'	Virial parameter corrected for carrier solubility effects	91
η	Carrier gas viscosity	17
η	Measure of peak asymmetry	28
λ	Packing geometry term in van Deemter equation	21
λ	Carrier-stationary phase solubility term	91
μ	Chemical potential	14
ν	Reduced linear carrier velocity	22
ρ_L	Stationary-phase density	19
σ	Peak standard deviation	21
σ	Surface tension	140
σ	Molecular cross-sectional area	221
τ_c	Sorbate monolayer weight	226
ϕ	Carrier-stationary phase solubility term	91
ϕ	Volume fraction	120
χ	Interaction parameter	120
Ω	Mass transfer non-equilibrium term in Giddings equation	22