

THE SHAPE OF THE ELUTION PEAKS IN GAS CHROMATOGRAPHY

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It is convenient to describe the shape of elution peaks by the *skew ratio*, R , defined as the ratio of the magnitudes of the slopes of the trailing and leading edges at their points of inflexion; thus when the trailing edge is steeper than the leading edge, the skew ratio is greater than unity.

Various theoretical treatments of gas-liquid chromatography (G.L.C.), using methods first developed for partition chromatography^{1,2}, start from the concept of the *distribution isotherm* which gives the concentration of the solute in the stationary phase as a function of the concentration of the solute in the moving (gas) phase. In the context of G.L.C. the distribution isotherm relates the concentration c of the solute in the liquid phase (expressed in moles per unit volume of the phase) to the *partial pressure* p of the solute, *cf. ref. 3, pp. 96 et seq.* According to both the "plate" treatment¹ and the "rate" treatment², the skew ratio should be unity if the distribution isotherm is linear, but should be less than unity if the distribution isotherm is concave towards the pressure axis and greater than unity if the isotherm is concave towards the concentration axis. The skew ratio is thus related to the *sign of the curvature*, $(d^2c/dp^2)_{p=0}$, of the graph of c against p near the origin:

$$R \gtrless 1 \text{ according as } \left(\frac{d^2c}{dp^2} \right)_{p=0} \gtrless \infty. \quad (1)$$

Until recently no experimental data have been available to test this prediction, but it has been generally accepted and extended in the following way (*cf. ref. 3, p. 154*). At low concentrations the mole fraction x of the solute in the liquid phase is nearly proportional to the concentration c , so it is assumed that the shape of the distribution isotherm (c vs. p) is essentially the same as that of the gas solubility (x vs. p) plot, which is linear if the system obeys Henry's law,

$$p = hx, \quad (2)$$

where h is the Henry's law constant, equal to the vapour pressure of the pure solute only if the solution is ideal over the entire concentration range*. Thus skew ratios greater than unity are said to be attributable to negative deviations from Henry's

* Although in Henry's original formulation⁶ of this law the solubility was expressed in terms of amount (presumably mass) per unit volume, the statement of the law in terms of mole fractions has become universal in all thermodynamic works since LEWIS AND RANDALL⁶.

law (x vs. p plot concave towards x axis) and *vice versa*. Furthermore, since negative deviations from Henry's law are often associated with positive deviations from Raoult's law (which may be stated as eqn. (2) but with h equal to the vapour pressure of the pure solute) and *vice versa*, the skew ratio might be expected to correlate with deviations from Raoult's law.

ASHWORTH AND EVERETT⁷ have measured the solubilities of a series of low molecular weight hydrocarbons (C_6 to C_8) in dinonyl phthalate and in squalane, and the same systems have since been studied by G.L.C.^{8,9} Only the solutions of the four normal alkanes and of 2,2-dimethylbutane in dinonyl phthalate show positive deviations from Raoult's law in the low solute concentration region. In the other systems, including all the solutions in squalane, there are *negative* deviations from Raoult's law and positive deviations from Henry's law over the whole of the concentration range ($0 < x < 0.1$) covered by the G.L.C. experiments. According to the foregoing argument, we should therefore expect skew ratios *less* than unity in these latter cases and that the skew ratio should *decrease* with increasing sample size. In fact, both in the work of EVERETT AND STODDART⁸ and more recent work in this laboratory⁹, while the value of the skew ratio obtained by extrapolating to zero sample size is always just less than unity*, the skew ratio always increases with increasing sample size, being in some cases greater than 3 for 10 μ l samples.

This apparent contradiction between theory and experiment has previously been remarked upon by FREEGUARD AND STOCK¹⁰, who have measured the vapour-liquid "isotherms" for these systems and found them all to be concave towards the concentration axis. FREEGUARD AND STOCK state that this is the normal shape of the isotherm for all solutions of vapours in involatile liquids except those showing unusually large negative deviations from Raoult's law. While this is generally true, the situation is complicated by the fact that FREEGUARD AND STOCK have plotted their "isotherms" in terms of the amount of solute per gram of solvent rather than per ml of solution. It is therefore worthwhile to examine again the question of the shape of the distribution isotherm, with the object of establishing rigorously its curvature, since this is the property which through eqn. (1) determines the skew ratio of the elution peaks.

The concentration of the solute in the liquid phase, defined as the number of moles of solute per unit volume of solution, is well approximated by

$$c = \frac{n}{n_s v_s + n v} \quad (3)$$

where n_s and n are the numbers of moles of solvent and solute respectively, and v_s and v are the molar volumes of pure solvent and solute respectively. (The approximation consists in ignoring the volume of mixing, which is always small in dilute solutions.) The relation between the concentration c and the mole fraction x of the solute, defined by

$$x = \frac{n}{n + n_s} \quad (4)$$

* The limiting value of the skew ratio is in every case between 0.80 and 0.85. The fact that it is less than unity is probably due to finite response times of the katharometer and recorder¹¹.

is then

$$cw_s = \frac{1}{1 - \alpha x} \quad (5)$$

where

$$\alpha = \frac{v_s - v}{v_s} \quad (6)$$

Combining eqn. (5) with eqn. (2) gives for the distribution isotherm of a solution obeying Henry's law

$$cw_s = \frac{p}{h - \alpha p} \quad (7)$$

The curvature of the isotherm is then not zero but

$$\frac{d^2c}{dp^2} = \frac{1}{w_s} \left[\frac{2\alpha h}{(h - \alpha p)^3} \right] \quad (8)$$

and at $p = 0$ has the value

$$\left(\frac{d^2c}{dp^2} \right)_{p=0} = \frac{2\alpha}{w_s h^2} = \frac{2}{w_s h^2} \left(\frac{v - 1}{v} \right) \quad (9)$$

where v_s/v has been set equal to v , the ratio of the sizes of the solvent and solute molecules, so that $\alpha = (v - 1)/v$. The limiting curvature of the distribution isotherm for a system obeying Henry's law is thus always positive unless $v > v_s$. It is extremely unlikely that the molar volume of any relatively involatile liquid suitable for use as the stationary phase in G.L.C. will be smaller than the molar volume of any relatively volatile solute which can be studied by this method. Consequently, *if a system obeys Henry's law we must expect G.L.C. elution peaks to have skew ratios greater than unity even at zero sample size.*

The confusion on this point has arisen because of the assumption that molal concentration \bar{c} , molar concentration c , and mole fraction x are linearly related at low concentration, *i.e.*,

$$\bar{c} \frac{M}{1000} \doteq cw_s \doteq \frac{p}{h} \quad (10)$$

instead of

$$\bar{c} \frac{M}{1000} = \frac{p}{h - \alpha p}; \quad cw_s = \frac{p}{h - \alpha p} \quad (11)$$

While the consequent error in c is trivial, that in the curvature d^2c/dp^2 is important.

The conditions under which a symmetrical peak is to be expected may be examined by expressing d^2c/dp^2 in terms of the activity coefficient, γ , of the volatile solute defined by

$$p = p^\circ \gamma x \quad (12)$$

where p° is the vapour pressure of pure solute ($x \rightarrow 1$).

Combining eqns. (5) and (12) gives, instead of eqn. (11),

$$cw_s = \frac{p}{p^\circ \gamma - \alpha p} \quad (13)$$

whence

$$\left(\frac{d^2c}{dp^2}\right)_{p=0} = \frac{2}{v_s(p^0\gamma^\infty)^2} \left[\alpha - p^0 \left(\frac{d\gamma}{dp}\right)_{p=0} \right]. \quad (14)$$

where γ^∞ is the value towards which γ tends as x tends to zero. Further, since

$$\frac{d\gamma}{dp} = \frac{d\gamma}{dx} \frac{dp}{dx},$$

while from eqn. (12),

$$\left(\frac{dp}{dx}\right)_{p=0} = p^0\gamma^\infty,$$

we find

$$p^0 \left(\frac{d\gamma}{dp}\right)_{p=0} = \frac{1}{\gamma^\infty} \left(\frac{d\gamma}{dx}\right)_{x=0}.$$

Thus $(d^2c/dp^2)_{p=0}$ is zero and $R = 1$ when

$$\left(\frac{d \ln \gamma}{dx}\right)_{x=0} = \alpha = \frac{\gamma - 1}{\gamma}. \quad (15)$$

In general, from eqns. (1) and (14)

$$R \gtrless 1 \text{ according as } \left(\frac{d \ln \gamma}{dx}\right)_{x=0} \gtrless \frac{\gamma - 1}{\gamma}. \quad (16)$$

For molecules of equal size $R = 1$ when $(d \ln \gamma/dx)_{x=0} = 0$, while for molecules of different sizes the limiting slope of $\ln \gamma$ against x must reach a sufficiently large value in the range 0 to 1. Since nearly all systems relevant to gas chromatography consist of mixtures of molecules of widely different sizes, it is of interest to see what predictions follow from the theories of such solutions.

We consider first athermal solutions. The statistical theory gives¹²

$$\gamma_{\text{ath}} = \frac{[\gamma - (\gamma - 1)x]^{\frac{1}{2}z-1}}{[q - (q - 1)x]^{\frac{1}{2}z}} \quad (17)$$

where z is the average number of nearest neighbours in the quasi-lattice of the liquid, and q is defined by

$$zq = z\gamma - 2\gamma + 2. \quad (18)$$

We shall assume that γ in these equations can be identified with that defined earlier by the ratio of the molar volumes of the components (*cf.* ASHWORTH AND EVERETT⁷).

Equation (17) can be written

$$\gamma_{\text{ath}} = \frac{\gamma^{\frac{1}{2}z-1}}{q^{\frac{1}{2}z}} \cdot \frac{(1 - \alpha x)^{\frac{1}{2}z-1}}{(1 - \beta x)^{\frac{1}{2}z}}, \quad (19)$$

where

$$\alpha = \frac{\gamma - 1}{\gamma}, \quad \text{as before; and} \quad \beta = \frac{q - 1}{q}. \quad (20)$$

Taking logarithms and differentiating we obtain

$$\frac{d \ln \gamma_{ath}}{dx} = \frac{1}{2} z \frac{\beta}{1 - \beta x} - \left(\frac{1}{2} z - 1\right) \frac{\alpha}{1 - \alpha x} \quad (21)$$

so that when $x \rightarrow 0$

$$\left(\frac{d \ln \gamma_{ath}}{dx}\right)_{x=0} = \left(\frac{r-1}{r}\right) \left(\frac{q-1}{q}\right). \quad (22)$$

Thus for athermal solutions

$$\left(\frac{d \ln \gamma_{ath}}{dx}\right)_{x=0} < \frac{r-1}{r} \quad \text{and} \quad R > 1. \quad (23)$$

If $z \rightarrow \infty$ and r is large (*i.e.*, the case of a high polymer solution in the Flory-Huggins approximation), $q = r$ and so

$$\left(\frac{d \ln \gamma_{ath}}{dx}\right)_{x=0} = \left(\frac{r-1}{r}\right)_{r \rightarrow \infty}^2 \simeq \left(\frac{r-1}{r}\right) \simeq 1 \quad (24)$$

and symmetrical elution peaks will be observed, at least for very small sample sizes. For non-athermal solutions, eqn. (17) must be multiplied by

$$\gamma_{th} = \exp \frac{w}{kT} \left[\frac{q(1-x)}{q - (q-1)x} \right]^2 \quad (25)$$

where w is the "interchange energy" defined by

$$w = z \{ \varepsilon^{*12} - \frac{1}{2}(\varepsilon^{*11} + \varepsilon^{*22}) \}, \quad (26)$$

and ε_{ij} are the pair interaction potentials¹². This leads to

$$\left(\frac{d \ln \gamma_{th}}{dx}\right)_{x=0} = -\frac{2w}{kT} \cdot \frac{1}{q} \quad (27)$$

and, adding this term to eqn. (22),

$$\left(\frac{d \ln \gamma}{dx}\right)_{x=0} = \left(\frac{r-1}{r}\right) - \frac{1}{q} \left(\frac{r-1}{r} + \frac{2w}{kT}\right). \quad (28)$$

Thus when w is positive, as was found for all the solutions studied by ASHWORTH AND EVERETT, the limiting slope of $\ln \gamma$ against x is even less than for the athermal case and the elution peaks will be more unsymmetrical.

Peak symmetry will be observed only when w has a negative value satisfying

$$\frac{2w}{kT} = -\left(\frac{r-1}{r}\right). \quad (29)$$

The occurrence of large negative values of w is in fact extremely rare and limited to mixtures with a highly polar component. Consequently, since most mixtures of

non-polar liquids of widely different molecular size are described with reasonable accuracy by the statistical theory of solutions, we conclude that the occurrence of skew ratios greater than unity must be regarded as normal in G.L.C. irrespective of the sign of moderate deviations from Henry's law.

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SUMMARY

An analysis is given of the relationship between peak shape and the deviation from ideality of the solution of vapour in the stationary phase. Earlier discussions have obscured the true situation by overlooking the mathematical consequence of assuming that the concentration of the solution is directly proportional to the mole fraction. A more rigorous analysis leads to a relationship between the nature of the peak asymmetry and the behaviour of the activity coefficient of the volatile solute in infinitely dilute solution. Comparison with the theory of mixtures of molecules of different sizes shows that asymmetry of the peak, with the slope of the trailing edge greater than that of the leading edge (skew ratio > 1), must be regarded as normal in gas-liquid chromatography irrespective of the sign of moderate deviations from Henry's law.

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