and therefore:

$$\text{d} \ln V_g{}^0/\text{d} \, (1/T) = \Delta H_v/R.\tag{4}$$

The calculation of ΔS_v is not clear either. It is well known that:

$$\Delta G^0 = - RT \ln K \tag{5}$$

where K is the thermodynamic distribution coefficient defined as the ratio of solute activity in the gaseous and liquid phases, respectively, and ΔG° is the change of the standard Gibbs free energy per mole of solute. When choosing as standard states the 1 atm perfect gas state for the solute in the gas phase and an extremely dilute solute in the solvent for the solute in the liquid phase, it may be written as[4]:

$$K = Py/x.\tag{6}$$

Combining eqns. (3), (5) and (6) we obtain for the standard molar entropy change:

$$\Delta S_v{}^0 = \Delta H_v{}^0/T + R \ln (R\,273/V_g{}^0 M_L),$$

which relation can hardly be correlated with:

$$4.57 \times \log V_g = \Delta S_v - (\Delta H_v/T).$$

Concerning the relation between reaction enthalpy and equilibrium constant K_a, it is necessary to keep in mind that the relation $-\Delta H_a = R \, \text{d}\ln K_a/\text{d}(1/T)$ becomes valid only when ΔH_a is a change of standard enthalpy, which makes it necessary to define the standard states. K_a should also be defined by activities rather than by concentrations, which will both differ for the two systems discussed.

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Comments on the standard addition method used in quantitative gas chromatographic analysis

Quantitative analysis by gas chromatography, using the standard addition method, is based on the relation between the chromatogram of the initial sample under analysis and the chromatogram of a blend of this sample and a defined added

quantity of the component to be determined. There are three versions of this well-known technique: (1) The areas (or heights) of chromatographic peaks of the component to be determined and the corresponding injected quantities of sample are measured; (2) peak areas (or heights) of the compound to be determined and the peak areas (or heights) of an appropriate reference compound, already present in the initial sample, are measured; (3) the same procedure is used as under (2), but the auxiliary reference compound is added to the initial sample.

In the last mentioned two cases, the auxiliary reference substance serves as a measure of the quantity of sample injected. General relations between the amount of substance analysed, present in the chromatographic zone and the area of the corresponding chromatographic peak[1], and mass balance, lead to the following equations:

Method (1)

$$g_i = \frac{W_s}{W_{(i)}} \frac{100}{\dfrac{A_i{}^* \cdot w_{(i)}}{A_i \cdot w_{(i)}{}^*} 1 + \dfrac{W_{(s)}}{W_{(i)}} - 1} \tag{1}$$

where g_i is the weight per cent of component i to be determined, $W_{(i)}$ and W_s are the weight of the initial sample and that of the standard substance added (as pure component i), $A_i{}^*$ and A_i are the respective peak areas (heights) of the component under analysis corresponding to the injection of a sample–standard blend and of the initial sample, $w_{(i)}{}^*$ and $w_{(i)}$ are the weight of the sample–standard mixture and the weight of the initial sample introduced.

Method (2)

$$g_i = \frac{W_s}{W_{(i)}} \frac{100}{\dfrac{A_i{}^* \cdot A_p}{A_i \cdot A_p{}^*} - 1} \tag{2}$$

where, in addition to the symbols already defined, $A_p{}^*$ and A_p are, respectively, the peak area (height) of the auxiliary reference compound corresponding to the injection of the sample–standard mixture and that pertaining to the injection of the initial sample.

Method (3)

The relation for calculation of g_i is identical with eqn. (2); the values of $A_i{}^*$, $A_p{}^*$ and A_i, A_p correspond, however, to the injection of the sample–auxiliary substance–standard mixture, and to the injection of a mixture of sample and auxiliary substance only.

It is worth mentioning that the corresponding equations quoted in the literature, are mostly erroneous including those used several years ago by the second author[2] of this paper. The only exception to this general inconsistency is the relation given by DAL NOGARE AND JUVET[3], which is correct and equivalent to eqn. (1). Besides this relationship, one can find in the literature the eqn.[2]

$$g_t = \frac{100\ g_s A_t}{A_t{}^* - A_t} \qquad\qquad\qquad\qquad\qquad\text{(a)}$$

which has been declared equal to (1), provided that the injections w_t and $w_t{}^*$ are of identical weight; g_s in (a) represents the weight per cent of the standard added to the mixture of sample and standard.

The equation:

$$g_t = \frac{100\ g_s A_t/A_p}{(A_t{}^*/A_p{}^*) - (A_t/A_p)} \qquad\qquad\qquad\qquad\text{(b)}$$

has also been suggested[2] as equivalent to (2). Relations (a) and (b) have been adopted by other authors[4,5]. In another paper[6] the equation:

$$g_t = g_s A_t/(A_t{}^* + A_t) \qquad\qquad\qquad\qquad\qquad\text{(c)}$$

is quoted as equivalent to (a), and:

$$g_t = \frac{g_s A_t/A_p}{(A_t{}^*/A_p{}^*) - (A_t/A_p)} \qquad\qquad\qquad\qquad\text{(d)}$$

as equivalent to (2).

In addition to eqns. (a)–(d) one can find the following equations[7,8]:

$$g_t = \frac{100\ g_s A_t}{(A_t{}^* A_p/A_p{}^*)\,(100 - g_s)} \qquad\qquad\qquad\text{(e)}$$

and

$$g_t = \frac{W_s}{W_t}\ \frac{100\ A_t}{A_t{}^* - A_t\,(A_p{}^*/A_p)} \qquad\qquad\qquad\text{(f)}$$

The errors introduced by using relations (a)–(f) can be illustrated by the following simple model.

Let us analyse a mixture containing by weight 25 % benzene, 25 % toluene and 50 % xylene. Let benzene be the component to be determined and toluene the auxiliary reference substance. When mixing the sample to be analysed with the standard (pure benzene) in the ratio of 1 : 1 by weight and injecting the same quantities (on a weight basis) of the initial sample and its blend with the standard substance, then, under these conditions, the products of peak area and appropriate correction factors are proportional to the weight percentages of the corresponding compounds. Let us, therefore, introduce directly weight percentages. A simple calculation using the above relations furnishes data, summarized in Table I.

f_b, f_t and f_x are conversion factors enabling one to express the peak areas of benzene, toluene and xylene in terms of quantitative data on a weight basis; $g_t{}^*$ stands for the weight percentages of the corresponding components in the mixture of initial sample with added standard. In Table II, the results are listed for the g_t of benzene, as calculated according to the above equations.

In cases (a) and (b), multiplication of the numerator by 100 is obviously superfluous and the relations are, nevertheless, incorrect. Correct results (agreeing

TABLE I

NUMERICAL DATA SUBSTITUTED FOR THE RESPECTIVE QUANTITIES INTO EQUATIONS (1), (2), (a)–(f)

	g_i	$g_i{}^*$	A_i	$A_i{}^*$	A_p	$A_p{}^*$
Benzene	25	62.5	$25f_b$	$62.5f_b$		
Toluene	25	12.5	$25f_t$	$12.5f_t$	$25f_t$	$12.5f_t$
Xylene	50	25	$50f_x$	$25f_x$		

$W_s/W_{(t)} = 1$; $g_s = 50$.

TABLE II

THE RESULTS OBTAINED BY SUBSTITUTING THE NUMERICAL DATA FROM TABLE I INTO THE RESPECTIVE EQUATIONS

	Equation							
	(1)	(2)	(a)	(b)	(c)	(d)	(e)	(f)
g_i	25	25	3333	1250	14.3	12.5	20.0	50

with the above assumptions) are obtained only when using eqns. (1) or (2) for the calculation, and, of course, also when proceeding according to the equation given by DAL NOGARE AND JUVET[3].

It is of interest to note how long these same and relatively obvious errors can be referred to, and what diverse forms they may acquire. A similar problem has been already pointed out in polarography[9], where the standard addition method is used more often than in gas chromatography. The standard addition method is advantageous, mainly when chromatographing a very complex mixture where no free space remains available for the peak of the standard, or for eliminating efficiently the socalled "matrix effects" (cf. ref. 10).

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