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DERIVATION OF THE DIFFERENTIAL HEAT OF DISSOLUTION OR ADSORPTION FROM GAS-LIQUID CHROMATOGRAPHIC MEASUREMENTS

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SUMMARY

Taking into account the non-ideality of the gas phase, this paper develops a theory for the determination of the differential heat of dissolution, ΔH_S, from gas-liquid chromatography measurements. When ΔH_S is determined over a small interval of temperature, the calculation of ΔH_S can be made from measurements of retention times only without using the retention volumes. Using a carefully designed equipment, an accuracy in ΔH_S of better than 1% could be reached when ΔH_S is measured over an interval of temperature of one degree.

INTRODUCTION

The activity coefficient, γ, is the primary point of comparison between solution thermodynamics theory and experimental results in gas-liquid chromatography (GLC). However, it is exceedingly difficult to measure γ with a good accuracy because of the many experimental parameters which have to be determined. For most of them an accuracy better than 0.5% is difficult to achieve, whereas retention times could be measured within 0.01%. Consequently, the direct accurate measurement of the differential heat of dissolution, ΔH_S, at infinite dilution from only measurements of retention times, could be interesting.

As is so often the case when a particular physical property is being measured, interference from other effects in the system under study must be taken into account. This applies to GLC because the retention is additionally affected by interactions in the gas phase so that a correction must be used. The error is otherwise in the range 1–5% for most systems encountered in GLC.

Usually, the excess enthalpy of mixing, ΔH_e, is derived from measurements of γ at two or more different temperatures. Extrapolation of the observed retention volumes to zero flow rate is required to determine the absolute retention volume; furthermore, a precise value of the amount of stationary phase is necessary to calculate the specific retention volume. Instead of this delicate method, this paper gives an accurate method for determining ΔH_S from only the retention times which are much easier to determine with a great accuracy.

THEORY

When the non-ideality of the gas phase is taken into account, it has been shown[1,2] that the actual partition coefficient, k_0, extrapolated to zero pressure from static measurements of vapour pressure, can be expressed by the relationship

$$\ln k_0 = \ln k_0^* - \frac{P_2^0}{RT}(B_{22} - V_2') = \ln k_0^* + \varphi \qquad (1)$$

where k_0^* is the partition coefficient between the liquid phase and an ideal carrier gas:

$$k_0^* = \frac{n_3' RT}{\gamma_2^0 P_2^0 V_3'} \qquad (2)$$

T = the column temperature (°K);
P_2^0 = the vapour pressure of the pure liquid solute at T;
B_{22} = the second virial coefficient of the pure gas solute at T;
V_2' = the molar volume of the pure liquid solute at T;
V_3' = the molar volume of the stationary phase at T;
γ_2^0 = the activity coefficient of the solute in the liquid phase extrapolated to zero pressure;
R = the ideal gas constant;
n_3' = the number of moles of stationary phase in the column.

In all the following, the subscripts 1, 2 and 3 correspond to the carrier gas, the solute and the stationary phase, respectively.

Thermodynamic theory[3] requires that

$$\frac{\mathrm{d}[\ln(\gamma_2^0 P_2^0)]}{\mathrm{d}T} = \frac{\Delta H_S}{RT^2} \qquad (3)$$

so that

$$\frac{\mathrm{d}\left[\ln\left(\frac{k_0^*}{T}\right)\right]}{\mathrm{d}\left[\frac{1}{T}\right]} = \frac{\Delta H_S}{R} - \frac{\mathrm{d}[\ln V_3']}{\mathrm{d}\left[\frac{1}{T}\right]} \qquad (4)$$

It has also been shown[1,2] that k_0 can be determined from chromatographic measurements by means of the relationship

$$k_0 = \frac{t_R' \cdot D_o \cdot j}{V_3'(1+\beta)} \qquad (5)$$

with

$$\beta = \frac{2 B_{12} - V_2'}{RT} P_o J(^4_3)$$

t_R' = the corrected retention time of the solute or difference between the solute and the air retention times;

D_o = the flow rate of the carrier gas measured at the outlet pressure P_o of the column and at the temperature T of the system;

j = James and Martin's coefficient;

$J\binom{4}{3}$ = the pure number $\frac{3[(P_i/P_o)^4 - 1]}{4[(P_i/P_o)^3 - 1]}$;

B_{12} = the second virial coefficient of the gas mixture. As a first approximation, $2\,B_{12} \simeq B_{11} + B_{22}$.

In the following, we shall assume that the column inlet and outlet pressures are carefully controlled. Accordingly, j is constant and does not change with variations in column temperature. Thus, from eqn. 5

$$\frac{d\left[\ln\left(\frac{k_0}{T}\right)\right]}{d\left[\frac{1}{T}\right]} = \frac{d\left[\ln\left(\frac{t_R'\cdot D_o}{T}\right)\right]}{d\left[\frac{1}{T}\right]} - \frac{d[\ln(1+\beta)]}{d\left[\frac{1}{T}\right]} - \frac{d[\ln V_3']}{d\left[\frac{1}{T}\right]} \tag{6}$$

Since usually P_o is 1 atm and the maximum value of β is $3\,P_oJ\binom{4}{3}\cdot 10^{-2}$, for the extreme case of carbon dioxide used as the carrier gas[1,2], it can be written from eqns. 1 to 6 that

$$R\,\frac{d\left[\ln\left(\frac{t_R'\cdot D_o}{T}\right)\right]}{d\left[\frac{1}{T}\right]} = \Delta H_S + R\,\frac{d\varphi}{d\left[\frac{1}{T}\right]} + R\,\frac{d\beta}{d\left[\frac{1}{T}\right]} = \Delta H_S + C_1 + C_2 \tag{7}$$

We shall now calculate these two correction factors C_1 and C_2.

Estimation of $C_1 = R\,\frac{d\varphi}{d\left[\frac{1}{T}\right]}$

φ has been defined in eqn. 1. The solute vapour pressure is usually well fitted by a Clapeyron's relationship in a narrow temperature range.

$$P_2^0 = \exp\left(-\frac{\Delta H_v}{RT} + A\right) \tag{8}$$

so that

$$\frac{dP_2^0}{d\left[\frac{1}{T}\right]} = -\frac{\Delta H_v}{R}\,P_2^0 \tag{9}$$

To calculate a correction term, eqn. 8 is convenient. For a more precise calculation the use of an Antoine's relationship may become necessary. This would introduce a term $T^2/(T + C)^2$ in eqn. 9. From Berthelot's state equation[4]

$$B_{22} = \frac{9\,RT_c}{128\,P_c}\left\{1 - 6\left(\frac{T_c}{T}\right)^2\right\} \tag{10}$$

so that

$$\frac{dB_{22}}{d\left[\frac{1}{T}\right]} = -\frac{27}{32}\,\frac{RT_c^3}{P_cT} \tag{11}$$

The variation in density of the pure liquid solute with temperature can be written[5]

$$\varrho = A - BT^* - \frac{C}{E - T^*} \tag{12}$$

(In ref. 5 the numerical values of A, B, C, E are given for T^* in °F and ϱ in g/cm³. In this paper T is always in °K). Thus

$$\frac{dV_2}{d\left[\frac{1}{T}\right]} = -\frac{9}{5} M \frac{T^2}{\varrho^2} \left(B + \frac{C}{(E - T^*)^2}\right) \tag{13}$$

Thus from eqns. 1 and 8–13

$$C_1 = R \frac{d\varphi}{d\left[\frac{1}{T}\right]} = P_2^0 (B_{22} - V_2') \left(\frac{\Delta H_v}{RT} - 1\right)$$

$$+ \frac{27}{32} \frac{P_2^0}{P_{c,2}} RT_{c,2} \left[\frac{T_{c,2}}{T}\right]^2 - P_2^0 \frac{9\,MT}{5\,\varrho^2} \left[B + \frac{C}{(E - T^*)^2}\right] \tag{14}$$

$$C_1 = K + L - N$$

Example: For hexane at $T = 69$°C, the vapour pressure derived from eqn. 8 is 1 atm.

$P_2^0 = 1$ bar; $P_{c,2} = 30.3$ bars; $T_{c,2} = 507$°K; $A = 0.7198$; $B = 46.10^{-5}$; $C = 12.6$; $E = 516.2$; $K \neq -296$ cal; $L \neq 62.5$ cal; $N \neq 1.68$ cal.
$C_1 \neq -235$ cal/mole, *i.e.* about 3% of ΔH_S.

Numerical values calculated from data in ref. 5 are given in Table I for other compounds.

TABLE I

CORRECTIONS[a] FOR NON-IDEAL BEHAVIOUR IN THE GAS PHASE[b]

Compounds	*Boiling point (°C)*	K	L	N	C_1	C_2	$\frac{dC_1}{dT}$	$\frac{dC_2}{dT}$
n-Hexane	69	296	62.5	1.68	−235	−102	−4.7	0.6
n-Nonane	150.7	417	85.1	2.99	−334	−134	−5.6	0.6
Cyclopentane	49.1	125	25.2	1.03	−101	−47.5	−2.2	0.3
Cyclohexane	80.6	268	56.1	1.27	−213	−92.1	−4.1	0.5
Benzene	80.0	238	48.9	1.01	−191	−81.1	−3.9	0.5
o-Xylene	144.3	386	77.6	1.63	−310	−122	−5.5	0.6

[a] K, L, N, C_1, C_2 in cal/moles; dC_1/dT, dC_2/dT in cal/mole × °K.
[b] The corrections are calculated at the boiling point of each compound.

Estimation of $C_2 = R \dfrac{d\beta}{d\left[\frac{1}{T}\right]}$

As it has been proved by the numerical example above, the contribution of the volume term is negligible so that

$$C_2 = P_o J\binom{4}{3} \left[B_{11} + B_{22} - V_2' - \frac{27\,R}{32\,T^2} \left\{\left(\frac{T_c^3}{P_c}\right)_1 + \left(\frac{T_c^3}{P_c}\right)_2\right\}\right] \tag{15}$$

Example: For hexane at $T = 69°C$ and $P_o J(\frac{4}{3}) = 1$ bar, with carbon dioxide as carrier gas, which is the most unfavourable case. $C_2 \# -102$ cal/mole, *i.e.* about 1% in ΔH_S. Numerical values are given in Table I for other compounds.

CALCULATION OF ΔH_S FROM RETENTION TIMES

Eqn. 7 shows that we could calculate ΔH_S from simple measurements of corrected retention times at various temperatures if we could assume that in an interval of temperature (T_1, T_2), very small compared to T, the RHS terms of eqn. 7 are constant. Let

$$\delta T = T_2 - T_1 \tag{16}$$

This will be proved below. Then, integrating this equation between temperatures T_1 and T_2

$$R \ln \frac{t_R'(T_1) \cdot D_o(T_2) \cdot T_1}{t_R'(T_2) \cdot D_o(T_1) \cdot T_2} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)(\Delta H_S + C_1 + C_2) \tag{17}$$

Over this small temperature interval, we can assume that the variation of viscosity with temperature is given by

$$\eta = K\, T^{5/6} \tag{18}$$

Among other types of equations that have been proposed, this equation gives the best results to take into account the change in viscosity with respect to temperature[6]. Over a small interval of temperature, the validity of this equation might be better than 0.1%.

From Darcy's law[6], it can be written

$$D_o(T) = \frac{\lambda}{2\eta L} \frac{P_i^2 - P_o^2}{P_o} \tag{19}$$

in which λ depends on the column permeability and gas crosssection. As we assume that the inlet and outlet pressures of the column are controlled at values independent of the column temperature, we have

$$\frac{D_o(T_2)}{D_o(T_1)} = \frac{\eta(T_1)}{\eta(T_2)} = \left(\frac{T_1}{T_2}\right)^{5/6} \tag{20}$$

and noting that

$$\ln\left(\frac{T_1}{T_2}\right) \# -\frac{\delta T}{T} \tag{21}$$

with an error of less than 0.15%. Then eqn. 17 becomes

$$\Delta H_S = \frac{-T_2^2}{\delta T} R \cdot \ln \frac{t_R'(T_1)}{t_R'(T_2)} + \frac{11}{6} R T_2 - (C_1 + C_2) \tag{22}$$

Whenever it is possible with a great precision to measure retention times at very close temperatures, eqn. 22 allows the calculation of ΔH_S. Moreover, if δT is sufficiently small, it becomes possible to carry out measurements of ΔH_S for different such small temperature intervals, and, thus, the variation of ΔH_S with respect to temperature can be studied.

We shall now discuss the validity of the assumption that the *RHS* terms of eqn. 7 are not temperature dependent in a small temperature range.

TEMPERATURE DEPENDENCE OF THE *RHS* TERMS OF EQN. 7

This is best studied by calculating the temperature coefficients of C_1, C_2 and ΔH_S.

Variation of C_1 with T

As shown above the variation of the volume term with T, in eqn. 14, can be neglected. We can write

$$C_1 = P_2^0 (B_{22} - V_2') \left(\frac{\Delta H_v}{RT_2} - 1\right) + \frac{27}{32} \frac{P_2^0}{P_{c,2}} RT_{c,2} \left(\frac{T_c}{T_2}\right)^2 \quad (23)$$

Differentiation of eqn. 23 gives

$$\frac{dC_1}{dT} = P_2^0 (B_{22} - V_2') \frac{\Delta H_v}{RT_2^2} \left(\frac{\Delta H_v}{RT_2} - 2\right) + \frac{27}{32} \frac{P_2^0}{P_{c,2}} R \left(\frac{T_{c,2}}{T_2}\right)^3 \left(\frac{2\Delta H_v}{RT_2} - 3\right) \quad (24)$$

This coefficient is usually small as shown by the following example.

Example: For hexane at $T_2 = 69$°C

$$\left|\frac{dC_1}{dT}\right| \# 4.6 \text{ cal/degree}$$

For $\delta T = 1$°C, this value results in a variation of about 2% of C_1 and less than 0.1% of ΔH_S. Other numerical results are given in Table I.

Variation of C_2 with T

Differentiation of eqn. 15 gives

$$\frac{dC_2}{dT} = \frac{81}{32} J(\tfrac{4}{3}) R \left\{\left(\frac{T_c}{T_2}\right)_1^3 \left(\frac{P_o}{P_c}\right)_1 + \left(\frac{T_c}{T_2}\right)_2^3 \left(\frac{P_o}{P_c}\right)_2\right\} \quad (25)$$

This coefficient is small because P_o is much smaller than P_c in most cases, whereas T_c/T_2 is most often smaller than 2.

Example: For hexane at $T_2 = 69$°C and $P_oJ(\frac{4}{3}) = 1$ bar with CO_2 as carrier gas

$$\left|\frac{dC_2}{dT}\right| = 0.6 \text{ cal/degree}$$

This is only 0.6% of C_2 and less than 0.01% of ΔH_S for $\delta T = 1$. With the more conventional carrier gases such as H_2, He, N_2 and A, this coefficient would be still smaller.

Variation of ΔH_S with T

Generally, over a large temperature range, ΔH_S decreases with increasing temperature at a rate of about 5 to 10 cal/degree. (From ref. 5 it results that the variations in ΔH_v are of this magnitude.) Thus the variation of the *RHS* of eqn. 7 is smaller than 20 cal, about 0.2% in ΔH_S for a temperature variation of 1°C. It will be shown in the next section that the error in the determination of ΔH_S which can be expected from a carefully prepared chromatographic apparatus is much larger than 0.2%.

Validity of Berthelot's state equation

Berthelot's state equation is a relationship with two constants. These constants can be determined for most components by applying the law of corresponding states which postulates that the ratio $P_c V_c / RT_c$ is constant for all compounds. This however is not true, and the ratio may vary in the range 5–10% for most hydrocarbons and carrier gases encountered in GLC (*cf.* Table II). Consequently an error of this order of magnitude on B_{11} or B_{22} may be expected.

TABLE II

COMPARISON BETWEEN THE EXPERIMENTAL AND CALCULATED VALUES OF THE SECOND VIRIAL COEFFICIENT[a]

Compound	*T (°K)*	*B_{22} (cm³)* Experimental	*B_{22}' (cm³)* Calculated	$\frac{B_{22} - B_{22}'}{B_{22}}$ (%)
Benzene	366.5	1046.6	945.2	4.5
	422.0	662.8	646.0	2.5
n-Hexane	366.5	1144.9	1029.9	11.2
	399.8	1039.2	849.5	18.9
Propylene	310.9	307.6	334.9	−8.4
	333.1	278.1	257.0	7.9
Acetylene	277.6	199.4	185.4	7.3
	294.3	167.9	161.8	3.6

[a] The calculated value is obtained from eqn. 10 and critical data from ref. 5. The observed value is derived from experimental data taken in ref. 9; $\log f/p$ is plotted *vs.* P and B_{22} calculated from the slope of the straight line obtained.

Table II shows a comparison between values of the second virial coefficient calculated by eqn. 10 for various compounds and values derived from experimental data on the compressibility of their vapour[9]. The accuracy of these experimental values may be estimated to 8%. The deviation is important only for *n*-hexane at 126°C, *i.e.* at temperatures much above the boiling point.

The data in Table II are in agreement with a possible error of 5 to 10% on B_{22}, arising from the use of eqn. 10. Since the correction terms C_1 and C_2 amount to about 4% of ΔH_S and depend mainly on B_{11} and B_{22}, the use of an approximative state equation introduces a systematic error of less than 0.4% in the measurement of ΔH_S.

PRECISION OF THE DETERMINATION OF ΔH_S

The temperature interval T_2–T_1 is very small; consequently $t_R'(T_1)$ and $t_R'(T_2)$ are very near. To derive the error on ΔH_S calculated from experimental data using eqn. 22, we shall let

$$t_R'(T_1) = t_R'(T_2) + \delta\tau \tag{26}$$

Expanding the logarithm in eqn. 22, we obtain

$$\Delta H_S \# \frac{-RT_2^2}{t_R'(T_2)} \cdot \frac{\delta\tau}{\delta T} + \frac{11}{6} RT_2 - (C_1 + C_2) \tag{27}$$

It is obvious that the preponderant error in ΔH_S comes from the $\delta\tau/\delta T$ terms which are both small differences between large quantities. If θ denotes absolute errors:

$$\frac{\theta\,(\Delta H_S)}{\Delta H_S} \# \frac{\theta\left(\dfrac{\delta\tau}{\delta T}\right)}{\dfrac{\delta\tau}{\delta T}} = \frac{\theta\,(\delta T)}{\delta T} + \frac{\theta\,(\delta\tau)}{\delta\tau} \tag{28}$$

The error on the absolute temperatures T_1 and T_2 may be 0.1°K because it is difficult to calibrate better a thermometer in the thermodynamical scale[7]. It is easier, however, to measure temperature differences, since the calibration error is then of the second order and the error on δT will be smaller than 0.01°C. The contribution to the error of temperature measurement to the error on ΔH_S could thus be smaller than 1%, as far as precise measurements of temperature differences are possible.

TABLE III

CRITICAL VALUE OF PV/RT FOR VARIOUS COMPOUNDS[8]

Methane	0.288	2,3-Dimethylbutane	0.269	Phenol	0.24
Nitrogen	0.292	Cyclopentane	0.276	Xylenol	0.38
Oxygen	0.300	1-Butene	0.277	Water	0.228
Hydrogen	0.305	Benzene	0.771	Methanol	0.224
Helium	0.305	Toluene	0.264	Ethanol	0.248
Argon	0.292	Ethylbenzene	0.263	1-Butanol	0.258
n-Hexane	0.264	*o*-Xylene	0.263	2-Propanone	0.236
n-Decane	0.246	*m,p*-Xylene	0.260	Ethyl acetate	0.253
3-Methylpentane	0.273	Methylchloride	0.276	Diethyl ether	0.259

With a carefully controlled precision equipment, it is possible to measure retention times with an accuracy of a few parts in 10^{-4} (ref. 7). If the relative error on t_R' is 3×10^{-4}, the absolute error on $\delta\tau$ will be $\theta\,(\delta\tau) = 6 \times 10^{-4}\, t_R'$. The absolute magnitude of $\delta\tau$ may be estimated from the conventional relationship

$$t_R' = k'\, t_m \tag{29}$$

where k' is the column partition coefficient and t_m the air retention time. If temperature varies slightly we shall assume that t_m remains constant in eqn. 29. This approximation is valid in an error calculation. Then

$$\delta\tau \simeq \frac{\delta t_R'}{\delta T}\,\delta T = \frac{\Delta H_S}{RT^2}\, k' t_m \delta T \tag{30}$$

Combining eqns. 29 and 30 gives

$$\frac{\theta\,(\delta\tau)}{\delta\tau} = 6 \times 10^{-4} \frac{RT^2}{\Delta H_S \delta T} \tag{31}$$

If $T = 350$°K, $\delta T = 1$°K and $\Delta H_S = 10^4$ cal/mole, we obtain a relative error on $\delta\tau$ of 0.75%. This precision could be improved by refining the methods of temperature control, temperature measurements and retention time measurements. Furthermore, systematic measurements of t_R *vs.* T at very small temperature intervals and statistical analysis of the data will still reduce the error. As shown by eqn. 31, however, a very good accuracy in the measurement of retention times is necessary if the value of ΔH_S is to be measured at various temperatures.

CONCLUSION

The method we have described here gives access to the value of the differential heat of dissolution, ΔH_S, from GLC measurements taking account of the effects of the gas phase non-ideality. The apparatus that is suggested should be able to reach an accuracy in ΔH_S better than 1% when ΔH_S is determined over a temperature interval of about one degree.

From the point of view of chromatography theory, one very interesting conclusion is that the method ought to be extended to the gas–solid chromatographic measurements as well. With respect to the precision achieved, it can be expected that the variation of the differential heat of adsorption with temperature should be significant enough to give access to the value of the partial molar heat capacity. In this way, information on the degree of freedom of the adsorbed molecule can be obtained.

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