# An Attempt at Interpretation of the Goulden Plot in Terms of an Isokinetic Relationship

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On the basis of precise $\nu_{OH}$ measurements and carefully checked p$K_a$ values the Goulden plot for substituted benzoic acids, acetylenic acids, and phenols has been reinvestigated: even for families of acids of similar structure the fit is not good. The same is found for the gas-phase p$K_a$ data. It is shown that the isokinetic temperature for the above acids is in the range $0 < \beta < T$; the dominant contribution to $\delta\Delta G$ comes from the $\delta\Delta S$ term. Moreover $\beta$ values for these reaction series are not constant which means there is a varying blend of $\delta\Delta H$ and $\delta\Delta S$ in $\delta\Delta G$. This in turn leads to deviations from the $\delta\Delta G$–$\nu_{OH}$ plot, since $\nu_{OH}$ is mostly related to internal changes in enthalpy.

GOULDEN has observed[1] that for various families of oxygen acids, a linear relationship between $\nu_{OH}$ and p$K_a$ holds. More recently this relationship was also studied by Exner.[2] Hepler *et al.*[3,4] have advanced a thermodynamic theory of dissociation of hydroxy- and carboxy-acids in which the square of the fundamental stretching frequencies $\nu^2_{OH}$ was taken as a direct measure of the internal enthalpy $\Delta H_{int.}$. On the other hand, in terms of internal and external contributions to enthalpy and entropy[3] and accepting Pitzer's assumption[5] that for ionic reactions $\delta\Delta S_{int.}$ is *ca.* 0, for acid–base dissociation one may write equation (1). Then, accepting

$$2.3\,RT\mathrm{p}K_a = \delta\Delta G^\circ = \delta\Delta H_{int.} + \delta\Delta H_{ext.} - T\,\delta\Delta S_{ext.} \quad (1)$$

that $\delta\nu_{OH}$ is a measure of changes in internal contributions to enthalpy, $\delta\Delta H_{int.}$, the Goulden plot (2) relates $\delta\nu_{OH}$ to the much more complex quantity p$K_a$.

$$\delta\nu_{OH} = g\mathrm{p}K_a + \text{const.} \quad (2)$$

Nevertheless it may be assumed that the slope $g$ of equation (2) should reflect the contribution of $\delta\Delta H_{int.}$ to $\delta\Delta G$ in (1). Recently, statistical methods[6-8] have been developed, allowing us to decide whether a given family obeys an isokinetic relationship and to estimate the isokinetic temperature $\beta$ [equation (3)] which in principle may be considered as a measure of the blend of enthalpy and entropy contributions to $\delta\Delta G$ [equation (4)]. In this paper we attempt to relate the Goulden plot to

$$\delta\Delta H = \beta\,\delta\Delta S \quad (3)$$

$$\delta\Delta G = \delta\Delta H - T\,\delta\Delta S \quad (4)$$

isokinetic properties of families of acids.

## RESULTS AND DISCUSSION

Table 1 presents $\nu_{OH}$ measurements of *m*- and *p*-substituted benzoic acids and phenols as well as of substituted acetylenic acids, all carried out in $CCl_4$, and p$K_a$ values carefully selected from the literature. Since $\nu_{OH}$ values are less complex quantities and more precisely measured than p$K_a$, the Goulden plot is calculated in a reverse way as (5).

$$\mathrm{p}K_a = \gamma\,\delta\nu_{OH} + \text{const.} \quad (5)$$

Table 2 presents the results of calculations for the above mentioned systems and also contains $\gamma$-values for benzoic acids in various media including the gas phase.

The difference in $\gamma$ for benzoic acids and two other systems studied in water is at the limit of the error of estimation. Unfortunately, estimates of isokinetic temperature, $\beta$, are also uncertain, and are all in the range 52—282 K. The situation is more advantageous in that for $\gamma$ values for benzoic acids in water, water–ethanol, ethanol, and dimethyl sulphoxide an increase is observed. Since in this series of solvents a decrease of solvation properties is expected one may assume that the $\delta\Delta G$ values reflect an increase in the $\delta\Delta H_{int.}$ contribution. This conclusion is supported by a very high value of $\gamma$ for gas-phase data, where the contribution of $\delta\Delta H_{int.}$ to $\delta\Delta G$ is predominant.[9] A similar finding has been made for phenols. This observation may help in better understanding the $\delta\Delta H_{int.}$, $\delta\Delta H_{ext.}$, and $\delta\Delta S$ contributions to $\delta\Delta G$ which in part may be deduced from the values of the isokinetic temperature, providing a reliable value of $\beta$ is estimated.

An immediate consequence of (3) and (4) is that for $|\beta/T| > 1$ the inequality (6) holds. It means that inside

$$|\delta\Delta H| > |T\,\delta\Delta S| \quad (6)$$

the range $|\beta/T| < 1$ the dominant contribution to $\delta\Delta G$ [equation (4)] is $T\,\delta\Delta S$. Unfortunately, none of the three systems studied in water [(1), (9), and (11) in Table 2] fulfils the requirement (6). Not only is $\beta$ not constant but also its probable value is in the range where dominant contributions to $\delta\Delta G$ are due to $\delta\Delta S$. This conclusion is in line with the findings of Hepler *et al.*,[11] Kebarle and McMahon,[9] and our earlier conclusions.[12]

In the case of ionic reactions, further analysis is possible. It was found[13] that the external isokinetic temperature[3,4] $\beta_{ext.}$ [equation (7)] is always positive.

$$\delta\Delta H_{ext.} = \beta_{ext.}\,\delta\Delta S_{ext.} \quad (7)$$

Making use of this, and of the Pitzer assumption[5] that $\delta\Delta S_{int.}$ *ca.* 0 for ionic reactions in solution, one may

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write a definition of the isokinetic temperature as in equation (8). Substituting $\delta\Delta S_{\text{ext.}}$ by $\delta\Delta H_{\text{ext.}}/\beta_{\text{ext.}}$, we

$$\beta = \frac{\delta\Delta H}{\delta\Delta S} \cong \frac{\delta\Delta H_{\text{int.}} + \delta\Delta H_{\text{ext.}}}{\delta\Delta S_{\text{ext.}}} = \beta_{\text{ext.}} + \frac{\delta\Delta H_{\text{int.}}}{\delta\Delta S_{\text{ext.}}} \quad (8)$$

$$\delta\Delta H_{\text{int.}} = \left(\frac{\beta}{\beta_{\text{ext.}}} - 1\right)\delta\Delta H_{\text{ext.}} \quad (9)$$

obtain equation (9) after simple rearrangement. This equation may be discussed in more detail. For $\beta < 0$ inequality (10) holds, with the immediate consequence that inequality (11) results. Thus we may conclude

$$\frac{\delta\Delta H_{\text{int.}}}{\delta\Delta H_{\text{ext.}}} < -1 \quad (10)$$

$$|\delta\Delta H_{\text{int.}}| > |\delta\Delta H_{\text{ext.}}| \quad (11)$$

that for $|\beta/T| > 1$ and $\beta < 0$ the dominant contribution to $\delta\Delta G$ is $\delta\Delta H$, within which the dominant contribution is $\delta\Delta H_{\text{int.}}$. Moreover $\delta\Delta H_{\text{int.}}$ and $\delta\Delta H_{\text{ext.}}$ are for $\beta < 0$ always opposite in sign. This latter conclusion agrees with an earlier statement [14] that for $\beta = 0$, $\delta\Delta H^\circ = 0$ or, in other words $\delta\Delta H_{\text{int.}} = -\delta\Delta H_{\text{ext.}}$.

Unfortunately, for $\beta > 0$ no firm conclusion may be drawn from equation (9) unless $\beta_{\text{ext.}}$, $\delta\Delta H_{\text{int.}}$, and $\delta\Delta H_{\text{ext.}}$ are known. However, the gas-phase measurements for benzoic acid [9] show $\Delta S^\circ$ low (due to rotation of $CO_2^-$ and $CO_2H$) and accordingly $\beta$ is positive and very high. For phenol $\Delta S^\circ$ is nearly zero and hence $\beta$ must be still higher than for benzoic acid. Because of inequality (6), this supports a higher gas-phase value of $\gamma$ for phenols than for benzoic acids. The variation in $\delta\Delta H$ for gas-phase measurements is very large,[9] and of the same sign as $\delta\Delta G$. It is likely that for solution measurements an increase of solute–solvent interactions expressed by $(\delta\Delta H_{\text{ext.}} - T\,\delta\Delta S)$ contributions are opposite in sign to $\delta\Delta H_{\text{int.}}$ since they lead to a decrease in $\delta\Delta G$, as shown by the decrease of $\gamma$ with an increase of the solvation power of solvents.

Finally the low accuracy of the linear regression (5) needs to be discussed. For p$K_a$ (in solution)–$\nu_{OH}$ plots it is clear that complex compensations between $\delta\Delta H_{\text{int.}}$, $\delta\Delta H_{\text{ext.}}$, and $\delta\Delta S$ may operate and they are undoubtedly responsible for the inaccuracy of the Goulden plot even within a family of compounds since $\beta$ is not constant for the families in question. It means that the blend of $\delta\Delta H$ and $\delta\Delta S$ may vary while going from one member to another within a family leading to various possible kinds of compensation as shown in relationship (12).

opposite in sign for $\beta < 0$ — in solution always of the same sign since $\beta_{\text{ext.}} > 0$

$$2.3\,RT\mathrm{p}K_a = \delta\Delta G = \underbrace{\delta\Delta H_{\text{int.}} + \delta\Delta H_{\text{ext.}}}_{\delta\Delta H} - T\,(\delta\Delta S) \quad (12)$$

of the same sign for $|\beta/T| > 1$ — of the same sign for $\beta > 0$ of opposite sign for $\beta < 0$

In the case of gas-phase data the inaccuracy of the linear regression (5) is also considerable. The reason may be that $\delta\nu_{OH}$ is a measure of the substituent effect on the elasticity of the O–H bond in the most harmonic part of the Morse curve, whereas $\delta\Delta G$, apart from a small $\Delta S^\circ$ term, is composed of the energy of dissociation into atoms (or more precisely into RO and H) and an electrostatic term. These two terms do not necessarily have to be related to each other in any simple way. The same is true for $\delta\nu_{OH}$ estimated for solution measurements.

Moreover, it should be pointed out that $\delta\nu_{OH}$

TABLE 1

$\nu_{OH}$ and p$K_a$ values for benzoic and acetylenic acids and phenols

| Acid<br>$XC_6H_4CO_2H$ [a]<br>X | $\nu_{OH}$/cm$^{-1}$ | p$K_a$ |
|---|---|---|
| *m*-$CH_3O$ | 3 539.7 | 4.093[11] |
| *m*-$CH_3$ | 3 540.7 | 4.269[18] |
| H | 3 539.9 | 4.202[19] |
| *m*-F | 3 536.1 | 3.865[11] |
| *m*-Cl | 3 535.1 | 3.834[11] |
| *m*-Br | 3 534.3 | 3.810[11] |
| *m*-I | 3 534.1 | 3.856[11] |
| *m*-CN | 3 530.7 | 3.596[18] |
| *m*-$NO_2$ | 3 530.3 | 3.460[11] |
| *m*-$COCH_3$ | 3 534.7 | 3.825[20] |
| *m*-CHO | 3 534.8 | 3.951[21] |
| *m*-OH | 3 538.1 | 4.076[11] |
| *p*-$NH_2$ | 3 547.4 | 4.83[22] |
| *p*-$CH_3O$ | 3 543.3 | 4.494[19] |
| *p*-OH | 3 542.8 | 4.590[18] |
| *p*-Bu$^t$ | 3 441.0 | 4.389[23] |
| *p*-Pr$^i$ | 3 541.3 | 4.354[24] |
| *p*-$CH_3$ | 3 542.0 | 4.370[19] |
| *p*-F | 3 538.5 | 4.141[24] |
| *p*-Cl | 3 536.7 | 3.969[19] |
| *p*-Br | 3 536.1 | 3.961[19] |
| *p*-I | 3 535.4 | 3.995[19] |
| *p*-CN | 3 530.7 | 3.55[18] |
| *p*-CHO | 3 535.1 | 3.75[21] |
| *p*-$NO_2$ | 3 528.9 | 3.424[19] |
| *p*-$COCH_3$ | 3 533.8 | 3.700[20] |
| $XC\equiv CCO_2H$ [b] | | |
| PhO | 3 524.5 | 3.09 |
| $CH_3$ | 3 523.7 | 2.656 |
| Ph | 3 521.3 | 2.253 |
| $(CH_3)_3Si$ | 3 519.3 | 2.205 |
| PhS | 3 518.8 | 2.11 |
| I | 3 514.9 | 2.002 |
| H | 3 518.1 | 1.940 |
| Br | 3 516.4 | 1.903 |
| Cl | 3 516.7 | 1.889 |
| $EtO_2C$ | 3 510.5 | 1.05 |
| $XC_6H_4OH$ [c] | | |
| H | 3 612.1 | 10.020[26] |
| *m*-$CH_3$ | 3 612.2 | 10.098[27] |
| *p*-$CH_3$ | 3 614.6 | 10.276[27] |
| *m*-Cl | 3 610.2 | 9.119[28] |
| *p*-Cl | 3 606.9 | 9.406[29] |
| *m*-Br | 3 606.2 | 9.031[28] |
| *p*-Br | 3 608.9 | 9.366[29] |
| *m*-F | 3 608.9 | 9.26[30] |
| *p*-F | 3 614.3 | 9.91[30] |
| *m*-$NO_2$ | 3 601.4 | 8.355[31] |
| *p*-$NO_2$ | 3 596.0 | 7.156[32] |
| *m*-$NH_2$ | 3 613.3 | 9.86[33] |
| *p*-$NH_2$ | 3 618.4 | 10.46[33] |
| *m*-$CH_3O$ | 3 612.4 | 9.65[30] |
| *p*-$CH_3O$ | 3 617.9 | 10.21[30] |
| *m*-$(CH_3)_2N$ | 3 614.0 | 9.22[34] |

[a] $\nu_{OH}$ taken from ref. 16*a*; reliable p$K_a$ chosen by following a suggestion made by Charton.[17] [b] p$K_a$ values taken from ref. 25; $\nu_{OH}$, this work. [c] $\nu_{OH}$ taken from ref. 16*b*.

is correlated with variations in internal enthalpy changes, which are those parts of $\delta\Delta H_{\text{int.}}$ which refer to variation in the internal enthalpy changes in the acid in equilibrium (13) where ROH and $RO^-$ are hydroxylic

$$ROH + H_2O \rightleftharpoons RO^- + H_3O^+ \qquad (13)$$

or carboxylic acids and their conjugated bases, respectively. Equation (14) applies and $\nu_{OH}$ refers only to

$$\delta\Delta H_{\text{int.}} = \delta H_{\text{int.}}(RO^-) - \delta H_{\text{int.}}(ROH) \qquad (14)$$

$\delta H_{\text{int.}}$ (ROH). The two elements of the right hand side of equation (14) are not necessarily related to each other in any simple way. The blend of inductive and resonance contributions to $\delta H_{\text{int.}}$ ($RO^-$) and $\delta H_{\text{int.}}$ (ROH) may differ, even considerably. This may be another source of inaccuracy in equation (5). The same is of course true for the gas-phase data, where additionally the contribution from the variation in polarizability has to be taken into account.

TABLE 2

Statistical characteristics of the Goulden plot for benzoic and acetylenic acids and phenols and some data for related relationships

| Ionization of | $n$ [a] | $r$ [b] | $\psi$ [c] | $\gamma$ | $\beta$/K |
|---|---|---|---|---|---|
| (1) Benzoic acids in water | 26 | 0.984 | 0.18 | 0.077(3) [d] | 72,[e] −40 [f] |
| (2) Reaction (1) in 33.2% ethanol–water | 12 | 0.995 [g] | | 0.10 [g] | |
| (3) Reaction (1) in 52% ethanol–water | 12 | 0.990 [g] | | 0.11 [g] | |
| (4) Reaction (1) in 73.4% ethanol–water | 12 | 0.991 [g] | | 0.12 [g] | |
| (5) Reaction (1) in 84.5% ethanol–water | 12 | 0.981 [g] | | 0.12 [g] | |
| (6) Reaction (1) in ethanol | 12 | 0.994 [g] | | 0.13 [g] | |
| (7) Reaction (1) in dimethyl sulphoxide | 11 | 0.973 [g] | | 0.19 [g] | |
| (8) Reaction (1) in the gas phase [l] | 17 | 0.917 | 0.41 | 0.58(6) [d,h] | large [m] |
| (9) Phenols in water | 16 | 0.957 | 0.30 | 0.14(1) [d] | −52 [i], 282 [j] |
| (10) Reaction (9) in the gas phase [l] | 15 | 0.963 | 0.28 | 1.01(9) [d,h] | very large [m] |
| (11) Acetylenic acids in water | 10 | 0.947 | 0.34 | 0.12(1) [d] | ~160 [k] |

[a] Number of experimental points. [b] Correlation coefficient. [c] Exner's GOF parameter, *cf.* ref. 35. [d] Standard deviation in parentheses. [e] Calculated by use of the calorimetric data of Hepler *et al.*[11]. [f] Estimated for narrow range of temperatures.[10] [g] Calculated by direct use of the Hammett equation since $\gamma$(solvent) = $\gamma$(water) × $\rho$(solvent). Reaction constants $\rho$(solvent) taken from ref. 36; correlation coefficient given for Hammett plot used to obtain $\gamma$. [h] Gas-phase data: $\delta\Delta G = D(\text{A–H}) - \text{EA(A)}$ where $D$(A–H) is bond dissociation energy and EA(A) electron affinity of A; $\delta\Delta G/2.303RT$ applied in calculation of $\gamma$. [i] Estimated for *m*-substituted phenols; few calorimetric measurements [37] support this value. [j] Methyl- and dimethyl-substituted phenols (including phenol itself); $\beta$ calculated from calorimetric measurements; [15] when only *m*- and *p*-substituted species are taken into account, $\beta$ = 280 K. [k] Approximate value, direct $\delta\Delta H°$ *versus* $\delta\Delta S°$ plot yields lack of any regularity. [l] Ref. 9. [m] Rough estimates based on data of ref. 9.

Finally, it may be concluded on the basis of equation (12) and the results of Table 2, that for measurements of $pK_a$ in less solvating solvents one may expect a greater and better defined value for $\beta$, since the ($\delta\Delta H_{\text{ext.}} - T\,\delta\Delta S$) term should play a less important role.

The most important conclusion may be expressed as follows. If the isokinetic relationship is fulfilled and all kinds of compensation in equation (12) are strictly linear, then even if $\delta\Delta H_{\text{int.}}$ is not the dominant contribution, it is collinear with $\delta\Delta G$, *i.e.* the quantity most often used to discuss substituent, reactant, or medium effects. If the isokinetic relationship is not fulfilled too precisely but $|\beta/T| \gg 1$ then, following equations (6) and (11), $\delta\Delta H_{\text{int.}}$ is the predominant contribution to $\delta\Delta G$ and any analysis of it in terms of purely electrical terms (inductive, resonance) is justified. If the isokinetic relationship is not fulfilled too precisely but $|\beta/T| < 1$ then $\delta\Delta H_{\text{int.}}$ is not an important contribution to $\delta\Delta G$, and any analysis of $\delta\Delta G$ in terms of electrical effects may be successful by chance, due to an unknown mechanism of mutual compensation between external ($\delta\Delta H_{\text{ext.}} - T\,\delta\Delta S$) and internal terms. Finally if the isokinetic relationship does not hold for a given reaction series it simply means that the blend of $\delta\Delta H$ and $\delta\Delta S$ in $\delta\Delta G$ is different for each member of the family, *i.e.* the contribution of $\delta\Delta H_{\text{int.}}$ varies considerably from one compound to another, within the reaction series. In this case any analysis based upon a concept of electric effects which are internal in their nature is not completely justified.

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