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Journal of Chromatography A, 946 (2002) 47–49

JOURNAL OF  
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

# Mechanistic implications of the equality of compensation temperatures in chromatography

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Received 13 June 2001; received in revised form 19 November 2001; accepted 19 November 2001

## Abstract

A common interpretation of the observation that two processes exhibit similar compensation temperatures in an enthalpy–entropy plot is that the two processes occur via the same “mechanism”. We show that this interpretation is not rigorously allowed. In fact, the only thing that can be concluded from the observation of identical compensation temperatures is that the relative contributions of enthalpy and entropy to the overall free energy are the same in the two processes. Since it is possible that two processes occur via different mechanisms that, by chance, result in the same relative blends of enthalpy and entropy, the observation of identical compensation temperatures cannot be used as evidence for mechanistic identity. If two processes exhibit different compensation temperatures, however, it can logically be concluded that the two processes are mechanistically distinct. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Compensation temperatures

## 1. Introduction

Enthalpy–entropy compensation refers to the experimental observation of a linear relationship between  $\Delta H^\circ$  and  $\Delta S^\circ$  for a specific type of process (e.g., a chemical reaction for a series of reactants). This phenomenon has been found in many different systems, including heterogeneous catalysis, diffusion in metals, ionic crystals and amorphous polymers, conduction in amorphous semiconductors, and phase equilibria between hydrophobic and hydrophilic phases and between multi-component fluid phases

[1–11]. The vaporization of a series of pure liquids at a given temperature is a good example where such compensation effects have been observed [12–14]. The relationship between the enthalpy of vaporization ( $\Delta H_{\text{vap}}^\circ$ ) of most pure liquids and their corresponding entropy of vaporization ( $\Delta S_{\text{vap}}^\circ$ ), where the standard states are the pure liquid and pure gas at 25 °C and 1 atm total pressure, is given by the following equation [13]:

$$\Delta H_{\text{vap}}^\circ (\text{J mol}^{-1}) = 806.5 \Delta S_{\text{vap}}^\circ (\text{J mol}^{-1} \text{K}^{-1}) - 43\,024 \quad (1)$$

where the units on the slope and intercept are K and J/mol, respectively. In general, enthalpy–entropy relationships take the form:

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$$\Delta H^\circ = \beta \Delta S^\circ + \alpha \quad (2)$$

Substituting for  $\Delta H^\circ$  in  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  gives:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = (\beta \Delta S^\circ + \alpha) - T\Delta S^\circ \\ &= (\beta - T)\Delta S^\circ + \alpha \end{aligned} \quad (3)$$

The slope ( $\beta$ ) of a plot of  $\Delta H^\circ$  versus  $\Delta S^\circ$  is known as the “compensation temperature”; it is also called the iso-equilibrium or the iso-kinetic temperature, and is denoted  $T_c$ . This temperature is a characteristic of the process, and at this temperature,  $\Delta G^\circ$  for all reactants undergoing the process is the same and equal to  $\alpha$ . At  $T_c$  the enthalpy and entropy changes “fully compensate” one another, and there is no change in  $\Delta G^\circ$  upon changing the reactant.

Processes having similar compensation temperatures are said to be related to each other in that they proceed via the same mechanism [10]. An alternate viewpoint, which we prefer, is that similar compensation temperatures for different systems *may or may not* mean that the processes occurring in the different systems are the same; however, if the compensation temperatures are *different*, then the mechanisms of the two processes must be different. Thus, enthalpy–entropy compensation studies may provide insight about the retention mechanism and the underlying physico-chemical processes in chromatography. For example, when the compensation temperatures under different chromatographic conditions (different stationary phases, eluents, pH, etc.) are significantly different, then one must conclude that the retention mechanisms under the different conditions are different.

Before continuing further, mention must be made of what is meant by the word “mechanism”. A common conception of chemical mechanisms is the sequence of bond rearrangements that occur during a chemical reaction. To chromatographers, however, this definition seems ill-suited. Rather, the word “mechanism” is typically used to describe the way(s) in which solutes are retained. This could refer to the location of retention (i.e., the solid stationary phase surface in NPLC or to the fluid bonded phase in RPLC), or it could refer to the driving force of retention such as intermolecular attractive forces with the stationary phase or repulsive forces with the mobile phase, in addition to the entropic forces layered on top of these enthalpic considerations. For

purposes of this article, we will largely be using a hybrid of these issues. For example, when we talk about mechanistic identity, we will be implying that the mode (adsorption versus partition, etc.), as well as the nature and extent of the intermolecular interactions by which solutes are retained, are identical. Mechanistic dissimilarity, therefore, will relate to situations in which retention is caused by different fundamental effects and/or by different types and extents of intermolecular interactions.

A detailed look at exactly what can be deduced about mechanisms from studies of compensation temperatures is required before insight into separation mechanisms can be gained from the analysis of compensation temperatures. In the following derivation, we show that only two conclusions about the mechanism of a process can be drawn from an analysis of compensations temperatures. Specifically, if two processes have identical compensation temperatures, all that can be said about the processes is that the fraction of the total free energy arising from the enthalpy contribution is the same in both processes. The same is also true for the entropy/free energy ratio. This is the only conclusion that can be rigorously drawn about the mechanisms of the processes in the case of identical compensation temperatures. From this, it cannot be definitively concluded that the mechanisms of the processes are identical. If, however, the compensation temperatures are different for two processes, then one can conclude that the mechanisms for the two processes must be different.

## 2. Thermodynamic derivations of the meaning of equivalent compensation temperatures

Eq. (3) can be written for any specific solute in a set of solutes that demonstrate enthalpy/entropy compensation. Taking the difference in  $\Delta G^\circ$  between two solutes yields:

$$\delta_i \Delta G^\circ = \delta_i \Delta H^\circ - T \delta_i \Delta S^\circ = (\beta - T) \delta_i \Delta S^\circ \quad (4)$$

where  $\delta_i$  denotes the change in  $\Delta G^\circ$ ,  $\Delta H^\circ$ , or  $\Delta S^\circ$  upon changing the solute. At the compensation temperature,  $\beta$  (or  $T_c$  as it is commonly denoted),  $\delta_i \Delta G^\circ = 0$  and  $T_c = \delta_i \Delta H^\circ / \delta_i \Delta S^\circ$ . Thus, if two pro-

cesses (denoted with subscripts “1” and “2”) have the same  $T_c$ , then:

$$\frac{\delta_i \Delta H_1^\circ}{\delta_i \Delta S_1^\circ} = \frac{\delta_i \Delta H_2^\circ}{\delta_i \Delta S_2^\circ} \quad (5)$$

We now consider the ratio  $\delta_i \Delta H^\circ / \delta_i \Delta G^\circ$  for any process. Using Eq. (4) and the relationship  $\delta_i \Delta H^\circ = \beta \delta_i \Delta S^\circ$  which results from Eq. (2), it can be shown that:

$$\frac{\delta_i \Delta H^\circ}{\delta_i \Delta G^\circ} = \frac{\beta}{\beta - T} = \frac{T_c}{T_c - T} \quad (6)$$

Thus, for two processes with the same compensation temperature, the following is true:

$$\frac{\delta_i \Delta H_1^\circ}{\delta_i \Delta G_1^\circ} = \frac{1}{1 - (T/T_c)} = \frac{\delta_i \Delta H_2^\circ}{\delta_i \Delta G_2^\circ} \quad (7)$$

Similarly, from Eq. (4):

$$\frac{\delta_i \Delta S_1^\circ}{\delta_i \Delta G_1^\circ} = \frac{1}{T_c - T} = \frac{\delta_i \Delta S_2^\circ}{\delta_i \Delta G_2^\circ} \quad (8)$$

From the previous two relationships, it also follows that for two processes with identical compensation temperatures:

$$\frac{\delta_i \Delta H_1^\circ}{\delta_i \Delta H_2^\circ} = \frac{\delta_i \Delta S_1^\circ}{\delta_i \Delta S_2^\circ} = \frac{\delta_i \Delta G_1^\circ}{\delta_i \Delta G_2^\circ} \quad (9)$$

### 3. Interpretation of identical compensation temperatures

This derivation shows that if the compensation temperatures for two processes are identical, all that can be concluded is that the fraction of the total free energy that arises from the enthalpy contributions is the same in the two processes. Similarly, the fraction of the total free energy arising from the entropy contributions is the same. From this, it cannot be concluded that the mechanisms of the two processes must be identical, since two different mechanisms could result in the same proportion of enthalpy and entropy relative to the overall free energy. Application of Occam's Razor suggests that it is reasonable to conclude that the two mechanisms are the same, and that lacking proof to the contrary, proposing that the two mechanisms could be different introduces

unnecessarily complex explanations [15]. However, doing so is outside the scope of explanation allowed by algebra and thermodynamics. Therefore, the observation of identical compensation temperatures for different processes, without further mechanistic information, cannot rigorously be interpreted as indicating mechanistic identity, albeit this is the simplest implication. In this context, mechanistic identity merely indicates that the fraction of  $\delta \Delta G^\circ$  due to  $\delta \Delta H^\circ$  is the same for the two processes.

### 4. Interpretation of different compensation temperatures

If two processes have different compensation temperature (i.e.  $T_{c1} \neq T_{c2}$ ), then it follows that the equalities in Eqs. (5) and (7)–(9) must be replaced with inequalities. In this case, one can rigorously conclude that the mechanisms must be different, since identical mechanisms would necessarily lead to identical relative contributions of enthalpy and entropy to the overall free energy.

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