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Application of scanning methods to distinguish between entropy and enthalpy driven phase transitions

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ABSTRACT

All phase transitions can be divided into enthalpy and entropy driven. The driving forces of phase transitions in aqueous soft matter systems can be resolved by applying scanning methods. In this review three experimental methods — sorption calorimetry, differential scanning calorimetry and humidity scanning quartz crystal microbalance with dissipation monitoring are described. Advantages and disadvantages of the methods are discussed. The driving forces of phase transitions can be directly measured using sorption calorimetry or calculated using van der Waals differential equation using experimental data obtained by other methods. The results of experimental studies show that in surfactant and lipid systems the phase transitions to phases with higher curvature are driven by enthalpy, while phase transitions to phases with lower curvature are driven by entropy.

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1. Introduction

In soft matter systems, for example liquid crystalline phases of surfactants or lipids, phase transitions can be caused by a thin balance between different forces. The driving forces of these transitions are not easily understood. Thermodynamics can help in understanding the driving forces of transitions by resolving their enthalpic and entropic contributions. In this paper, experimental methods that allow distinguishing between enthalpy and entropy driven phase transitions are discussed. The methods described in this paper are scanning methods i.e. they allow continuous scanning of water content or temperature, which is needed for calculation of derivatives of thermodynamic parameters. Results of application of sorption calorimetry for resolving the driving forces of phase transitions in surfactant and lipid systems are reviewed. As an introduction to the topic, Section 2 discusses the concept of driving forces with illustrations from systems with chemical reactions and unary systems with phase transitions.

2. Thermodynamics of phase transitions

2.1. Driving forces in chemical reactions

When a spontaneous transition between two distinctly dissimilar states occurs, it is accompanied by a finite change of Gibbs energy ΔG. This change must be negative if the process is spontaneous. Alternatively, it can be said that a negative ΔG drives the transition. A simplest example that can illustrate it is a system with a chemical reaction A ↔ B. The transformation of molecule A to molecule B *on the level of individual molecules* (micro-level) can be described by the reaction coordinate [1] that characterizes for example differences in geometries of molecules A and B. The dependence of Gibbs energy in this transformation can be illustrated by a typical curve presented in Fig. 1 (left). When talking about an *ensemble of molecules* (macro-level) the transformation is described by the extent of reaction ξ. This parameter does not characterize individual properties of molecules but rather the amounts of molecules of types A and B:

$$d\xi = -dn_A = dn_B. \tag{1}$$

The dependence of the Gibbs energy of the system on the extent of reaction has a minimum due to entropy of mixing, see Fig. 1 (right).

In many areas of science, especially in mechanics, the concept of energy is closely connected to the concept of force, where force is defined as a negative of the derivative of energy with respect to coordinate x:

$$F = -\frac{dE}{dx}. \tag{2}$$

Analogously, generalized forces can be introduced in thermodynamics and kinetics when an appropriate coordinate is defined. If the coordinate is the reaction coordinate, then so-called reaction forces can be defined [2]. If the coordinate is the extent of reaction ξ, then the

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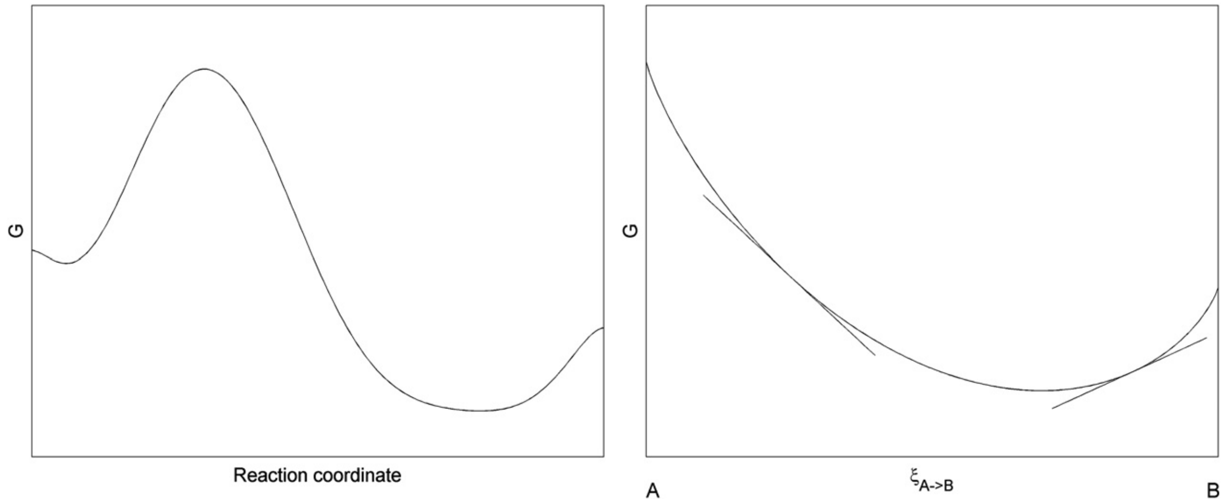

Fig. 1. The Gibbs energy in a system with chemical reaction as a function of reaction coordinate (left) and as a function of extent of reaction (right). The slopes of tangent lines (taken with negative signs) define the driving forces of reactions.

derivative of Gibbs energy will be the difference of chemical potentials of the two components [3]:

$$\left(\frac{dG^{ext}}{d\xi}\right)_{T,P} = \mu_B - \mu_A. \tag{3}$$

This difference of chemical potentials defines the reaction Gibbs energy $\Delta_r G$ at given composition (should not be confused with the standard reaction Gibbs energy $\Delta_r G^0$ related to properties of pure components). De Donder [4] and later Prigogine [5] used the derivative of Gibbs energy with respect to ξ to define affinity *A*. Hillert [6] used the term driving force *D* instead of affinity *A* to apply this concept for a wider range of processes. One should note that De Donder defined affinity as negative of the derivative of *G*. In the following text we use positive derivatives (like in Eq. (3)) in order to maintain the same sign of Gibbs energy changes and the driving forces.

Being a derivative of Gibbs energy with respect to a coordinate, $\Delta_r G$ has here a meaning of force. The Gibbs energy of any process can be considered as containing an enthalpy and an entropy contribution:

$$\Delta G = \Delta H - T\Delta S. \tag{4}$$

Hence the reaction Gibbs energy (which has a meaning of force) can also be separated into enthalpic and entropic contributions, both having meanings of forces. The balance between the two forces will determine the direction of the reaction in the same way as in mechanics a balance of two forces will determine the total force and the direction of movement. The enthalpy–entropy balance, in general case, results in a non-zero total force (reaction Gibbs energy) which will lead to a spontaneous reaction (a shift along the *x*-axis).

2.2. Phase transitions in unary systems

In the case of phase transformations the situation is different. Most often phase transitions are not experimentally studied as spontaneous processes between two distinctly different states separated by a finite Gibbs energy change. In experimental studies, especially when scanning methods are used, phase transitions are typically observed as a response of a system to an equilibrium change of its thermodynamic parameters, such as temperature or composition. In such processes the system is at (or close to) equilibrium during the whole transformation and therefore no finite changes of Gibbs energy can be observed. As an example, a phase transition caused by temperature change in one-component system is shown in Fig. 2.

At the point where the two lines cross, the Gibbs energies of the two phases are equal ($\Delta G = 0$), therefore

$$\Delta H = T\Delta S. \tag{5}$$

In an equilibrium process the transition follows the solid line shown in Fig. 2, being at lowest Gibbs energy possible at a given temperature. If because of some reason the equilibrium phase transition does not occur, then the system continues along the dashed line at temperatures higher than the phase transition temperature T^0. In that case the Gibbs energy change of the transition from first to second phase is negative ($G^{(2)} - G^{(1)} < 0$) and a spontaneous transformation from phase (1) to phase (2) is expected. Then, in a same manner as for chemical reaction, one can introduce a coordinate that describes the progress of the phase transition in such non-equilibrium isothermal process:

$$d\xi^{1\rightarrow 2} = dn^{(2)} = -dn^{(1)}. \tag{6}$$

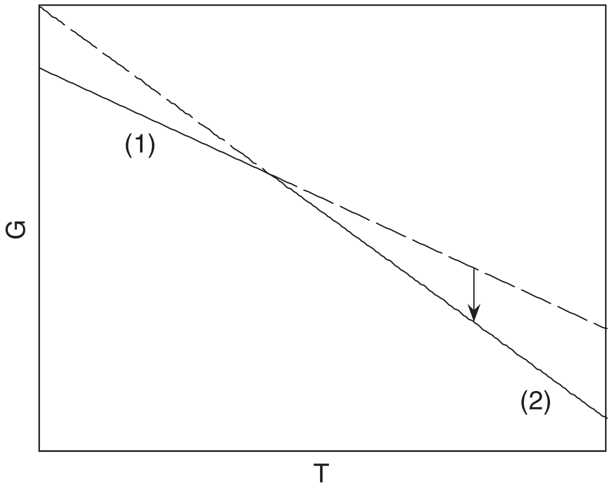

Fig. 2. The Gibbs energies of two phases involved in a temperature-induced phase transition in 1-component system. An equilibrium phase transition goes along the solid line. The arrow shows the Gibbs energy change in a spontaneous non-equilibrium transition from phase (1) to phase (2).

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