

TEMPERATURE BEHAVIOR OF ADSORPTION AS DESCRIBED BY THE GENERALIZED FRUMKIN ISOTHERM

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A theory describing the discontinuous changes in the degree of coverage which occur upon temperature variation in adsorption systems of particles interacting at the surface is developed. Many possible forms of temperature behavior of the systems are predicted as functions of their characteristic parameters.

Research into the adsorption of particles from the gas phase and from solution has a long history. An appreciable number of different isotherms have been suggested to describe the adsorption; they are based on certain models for the properties of surface and adsorbing particles, and also on certain assumptions of a mathematical nature [1-9]. Interaction between the adsorbing particles themselves, which gives rise to qualitatively new effects, was first taken into account by Frumkin [10] in an adaptation of the Langmuir isotherm. In the following, interactions were similarly taken into account in a number of other, more complicated isotherms [11-13]. It was found that attractive interaction of the adsorbed particles can lead to a discontinuous change in the degree of coverage, θ ($0 \leq \theta \leq 1$), relative to the concentration (pressure) of the adsorbing particles in the solution (gas). Recently it has been shown, in addition, that a number of highly nontrivial special features can also be expected when examining the dependence of θ on temperature [14]. It is the aim of the present communication to describe the results of a theoretical analysis of the temperature behavior of an adsorption system of particles interacting at the surface.

Consider a system which is described by the generalized Frumkin isotherm†

$$\frac{\theta}{m(1-\theta)^m} = Bce^{a\theta}. \quad (1)$$

Here $m > 1$ is the number of adsorption sites taken up on the surface by one adsorbed particle; c is the particle concentration in the bulk of the solution; $a > 0$ is the attraction constant describing the interaction between the adsorbed particles, and $B = \chi e^{-w/kT}$ where $w \geq 0$ is the energy change of a particle during adsorption; k is the Boltzmann constant; T is the absolute temperature; χ is a constant which is independent of θ and c , and which is related to the entropy change of a particle during adsorption; quantity a can also be written down as $a = \lambda/kT$ where $\lambda > 0$ is independent of temperature. For $m=1$, expression (1) changes to the widely known Frumkin isotherm [10]:

$$\frac{\theta}{1-\theta} = Bce^{a\theta}. \quad (2)$$

For the sake of definition, systems will be analyzed below which are described by isotherms (1) and (2), but the basic results can be applied to a very broad class of adsorption systems with interaction of the particles.

For sufficiently large a , the dependence of θ on c as defined by isotherms (1) and (2) has an S-shaped section (see Fig. 1). As a result, θ is monotonously increasing with increasing c , then it jumps at $c = c_{cr}$, and thereafter, $\theta(c)$ again increases monotonously. The value of c_{cr} is governed by the "rule of areas", which in effect means equality of the free energies of the adsorption system before and after the jump in θ (Fig. 1). The free energy, F , of the system (1)-(2) can be obtained, in particular, when using the mean-field approximation for the interaction energy and the methods of combinatorics for calculating the configurational entropy:

† Isotherm (1) is also called the Flory-Huggins isotherm, since it can be obtained in the context of a lattice model similar to that used by these authors in describing the properties of polymer chains in solutions [15, 16].

$$F(\theta) = W\theta - \lambda\theta^2/2 - kT\{\theta[1-m+\ln(m\rho)] - \theta \ln \theta - m(1-\theta) \ln(1-\theta)\}, \quad (3)$$

where $\rho \equiv xc$; the concentration c is here defined as the ratio between the number of adsorbing particles in the bulk of the solution and the number of solvent molecules. Equation (1) is obtained with the aid of (3) from the condition of minimum free energy, and can be transformed to

$$\frac{kT}{\lambda} = \frac{\tilde{\theta} - \theta}{\ln[\rho m(1-\theta)^m/\theta]}, \quad (4)$$

where $\tilde{\theta} \equiv W/\lambda$ ($-\infty < \tilde{\theta} < \infty$). Relations (3) and (4) completely define the temperature behavior of the system. Similar relationships had been examined in [17, 18] when analyzing phase transitions in asymmetric, disordered systems.

In certain ranges of parameters ρ and $\tilde{\theta}$, Eq. (4) has only one solution at some T , and three solutions ($0 \leq \theta_1 \leq \theta_2 \leq \theta_3 \leq 1$) at other T ; see Fig. 2. The lowest (θ_1) and highest (θ_3) of the solutions of Eq. (4) correspond to minima, the intermediate solution (θ_2) corresponds to a maximum in $F(\theta)$. In thermodynamic equilibrium, the system will be found in that state, out of the two given by θ_1 and θ_3 , which corresponds to the deeper minimum of $F(\theta)$. The state corresponding to $\theta = \theta_2$ is thermodynamically unstable. Under the condition $F(\theta_1) = F(\theta_3)$ a phase transition, $\theta_1 \rightarrow \theta_3$ or $\theta_3 \rightarrow \theta_1$, is realized. By putting quantities $\theta_{1,3}(T, \tilde{\theta}, \rho, \lambda, m)$ into the equality $F(\theta_1) = F(\theta_3)$ one determines the temperature of the phase transition, which in the present case is displayed as discontinuous change in the degree of coverage.

It follows from (4) that at specified m , the temperature behavior of adsorption is completely defined by the two parameters $\tilde{\theta}$ and ρ (parameter λ only specifies the scale of temperature variation). Accordingly, it will be convenient to characterize the system by a point in the plane of parameters $(\tilde{\theta}, \rho)$. The temperature behavior of adsorption turns out to be substantially different, depending on the position of this point in the plane $(\tilde{\theta}, \rho)$. It turns out that eight different kinds of $\theta(T)$ dependence can be realized, which are presented schematically in Fig. 2; these eight kinds of dependence correspond to eight regions in the plane of parameters $(\tilde{\theta}, \rho)$, see Fig. 3. Referring, for a mathematical description, to [14] we shall concentrate here on a detailed qualitative presentation of the picture that is obtained.

The plane of parameters $(\tilde{\theta}, \rho)$ is cut up into eight regions by the three critical curves ρ_I , ρ_{II} , and ρ_{III} and by the vertical $\tilde{\theta} = 0.5$. Curve ρ_I corresponds to the emergence (or disappearance) of S-shaped sections on the $\theta(T)$ curves (these sections are present in diagrams 2, 4, and 7 of Fig. 2). Curve ρ_{II} corresponds to the emergence (or disappearance) of double transitions, of the type shown in diagram 5 of Fig. 2. Curve ρ_{III} characterizes the disposition of loops in the $\theta(T)$ dependence: in the part of plane $(\tilde{\theta}, \rho)$ located to the left of curve ρ_{III} , loops are in the lower part (diagrams 1, 2, 5, and 6 of Fig. 2); in the part of plane $(\tilde{\theta}, \rho)$ located to the right of curve ρ_{III} , loops are in the upper part (diagrams 3, 4, 7, and 8 of Fig. 2). All three curves intersect in the single point $\theta = \theta_* = (1 + \sqrt{m})^{-1}$ and $\rho = \rho_* = \theta_*/m(1 - \theta_*)^m$. The vertical $\tilde{\theta} = 0.5$ characterizes the low-temperature state of the system: in the part of plane $(\tilde{\theta}, \rho)$ located to the left of this vertical, the degree of coverage tends toward unity in the region of low temperatures; in the part of plane $(\tilde{\theta}, \rho)$ located to the right of this vertical, the degree of coverage tends toward zero in the region of low temperatures.

Let us now discuss the temperature behavior of adsorption in each of the eight regions indicated. We shall begin with regions 1 to 5 which are located to the left of the vertical $\tilde{\theta} = 0.5$. These regions are characterized by the fact that $\theta \rightarrow 1$ when $T \rightarrow 0$. In region 1, which is located to the left of curves ρ_I and ρ_{II} and of the vertical $\tilde{\theta} = 0.5$, transitions are lacking, and θ diminishes monotonously from $\theta = 1$ at $T \rightarrow 0$ to $\theta = \theta_\infty$ at $T \rightarrow \infty$; one can see from (4) that quantity θ_∞ is defined by the relation† $\rho m(1 - \theta_\infty)^m = \theta_\infty$. The $\theta(T)$ dependence in region 1 is presented schematically in diagram 1 of Fig. 2. By crossing curve ρ_I we get from region 1 into region 2. Under these conditions an S-shaped section emerges on the $\theta(T)$ dependence, see diagram 2 of Fig. 2. A jump in θ is realized with increasing temperature in the S-shaped section. This jump is a "weak" one (the change in the degree of coverage, $\theta_3 - \theta_1$, is much less than unity) in the immediate vicinity of curve ρ_I (which is the locus of emergence of the S-shaped section), and "becomes stronger" as one moves away from curve ρ_I .

By crossing curve ρ_{III} , which corresponds to upward transition of the loop, we get into region 3 (see diagram 3 of Fig. 2); this region is bounded by curves ρ_{III} and ρ_I and by the vertical $\tilde{\theta} = 0.5$. We note that the

† The limits $T \rightarrow 0$ and $T \rightarrow \infty$ are, of course, discussed in a purely formal way, and need not actually be realized for the experimental observation of the effects being discussed; it is merely necessary that the transition temperatures be found within the temperature range where the adsorption system is existing.

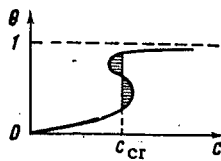


Fig. 1. The $\theta(c)$ dependence defined by Eqs. (1) and (2); the shaded areas are equal.

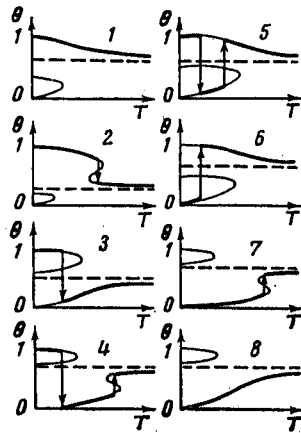


Fig. 2

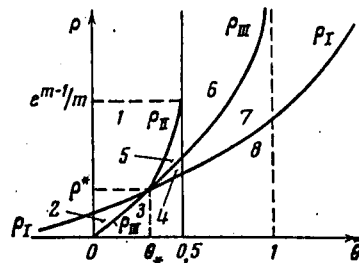


Fig. 3

Fig. 2. The different types of $\theta(T)$ dependence which are defined by Eq. (4). Arrows show the transitions between states; bold lines on the sections show solutions which are realized; dashed lines correspond to $\theta = \theta_\infty$. The numbers correspond to the regions in the plane of parameters $(\tilde{\theta}, \rho)$ in Fig. 3.

Fig. 3. The plane of parameters $(\tilde{\theta}, \rho)$.

jump in θ cannot occur via the asymptotic value $\theta = \theta_\infty$ at $T \rightarrow \infty$ in the phase transition in the S-shaped section, as it did, e.g., in region 2 (even though the difference $\theta_3 - \theta_1$ is not necessarily small in such a transition). In region 3, the phase transition involves the loop. In the general case, such a transition is necessarily attended by a jump across the value $\theta = \theta_\infty$; following [17, 19], we shall use the term 'supertransitions' for transitions of this type. Thus, one transition, which is a supertransition, is realized in region 3; it can be "strong" ($\theta_3 - \theta_1 \approx 1$) when $\tilde{\theta}$ is close to 0.5, and it can be "weak" ($\theta_3 - \theta_1 \ll 1$) when $\tilde{\theta}$ is close to θ_* and ρ is close to ρ_* .

By crossing curve ρ_I we move from region 3 to region 4. In this crossing, a weak transition arises; hence when reaching the region 4 we "acquire" a second transition which is independent of the first transition, and is related to the appearance of an S-shaped section in the lower branch of the $\theta(T)$ curve, see diagram 4 of Fig. 2. As a result, two independent transitions are realized with changing temperature in region 4; one of these transitions is a supertransition.

By crossing curve ρ_{III} we get from region 4 into region 5, which is bounded by curves ρ_{III} and ρ_{II} and the vertical $\tilde{\theta} = 0.5$. This region is remarkable insofar as a bitransition is realized here in the general case, which represents a pair of supertransitions, see diagram 5 of Fig. 2. The existence of bitransitions in two-level disordered systems was first predicted in [17]. Lastly, by crossing curve ρ_{II} we again reach region 1. One can see when comparing diagrams 1 and 5 of Fig. 2 that the $\theta(T)$ curves in regions 1 and 5 are topologically equivalent; the pair of supertransitions existing in region 5 is moving closer together as one approaches curve ρ_{II} , and vanishes when this curve is crossed.

Let us now turn to the case of $\tilde{\theta} > 0.5$. It had already been pointed out that here θ is close to zero in the region of low temperatures. In region 6, described by diagram 6 of Fig. 2, the $\theta(T)$ curves are topologically equivalent to the curves in regions 1 and 5, but the starting point here is the point $\theta = 0$. Hence with increasing T , one supertransition is realized here, which is attended by a discontinuous increase in θ . (We recall that on

the curves of similar shape in region 1, transitions are absent, while a bitransition exists in region 5.) In region 7, described by diagram 7 of Fig. 2, the $\theta(T)$ curves are equivalent to the corresponding curves of region 4, but here only one transition exists now, which is in the S-shaped section of the lower curve. Finally, in region 8, the system is found on the lower curve at all temperatures, and transitions are lacking, see diagram 8 of Fig. 2.

By examining the condition under which a phase transition is realized, viz., $F(\theta_1) = F(\theta_2)$, where $F(\theta)$ is defined according to (3) while θ_1 and θ_2 are the solutions of Eq. (4), one can obtain the expressions for the temperatures of weak ($T^{(w)}$) and strong ($T^{(s)}$) ordinary transitions in an explicit form†:

$$kT^{(w)} = \frac{\lambda(\bar{\theta} - \theta_*)}{\ln(\rho/\rho_*)}; \quad kT^{(s)} = \frac{\lambda(\bar{\theta} - 1/2)}{\ln(m\rho) - m + 1}. \quad (5)$$

In the case of a strong bitransition, the temperatures of the left-hand and right-hand transition (see diagram 5 of Fig. 2) are found to be equal:

$$kT^{(s,l)} = \frac{\lambda(\bar{\theta} - 1/2)}{\ln(m\rho) - m + 1}; \quad kT^{(s,r)} = \frac{\lambda(\bar{\theta} - 1)}{\ln\{m\rho[m - 1 - \ln(m\rho)]^m\}}. \quad (6)$$

In conclusion we shall formulate the special features found above for the temperature behavior of adsorption systems with interaction between the adsorbed particles. In doing so we point out that one can show that the results obtained are of a more general character, even though we have analyzed isotherms (1) and (2) in the present work, in order to be specific. Comparing Figs. 1 and 2 one sees that the temperature behavior, $\theta(T)$, has much more interesting and diverse possibilities than $\theta(c)$. A qualitatively new feature is the possibility that supertransitions are realized here, so that different sections of the $\theta(T)$ dependence are found on different sides from the asymptotic line θ_∞ . Double transitions can also be realized in the system: with increasing temperature one finds discontinuous desorption, but then, at some higher temperature, discontinuous adsorption. The last-mentioned effect, which is tied to the existence of double transitions, may be displayed by asymmetric systems. It occurs, in particular, with isotherm (1), where the region of double transitions is wider the larger m . With isotherm (2), one has $\theta_* = 0.5$ (a symmetric system); the interval $[\theta_* \dots 0.5]$ contracts into a point, and double transitions are lacking.

It is important to note that in adsorption studies in electrochemical systems, one has the possibility of controlling the system parameters by variation of the concentration of adsorbing particles and of the electrode potential, and can in this way realize the conditions under which the effects predicted will be displayed.

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† Printing errors which are eliminated in the present work appear in relations (8) and (9) of [14] for the quantities reported in (5) and (6).

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STATISTICAL THEORY OF ION SOLVATION IN ELECTROLYTE SOLUTIONS

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The concept of a structural solvent in the statistical mechanics of electrolyte solutions is discussed. Allowance for discrete solvent structure is based on a general analysis of the configuration integral of the whole system (solvent and solute) and on the representation of the term involving the interaction energy of the two initial subsystems in the configuration integral of the system by means of Maier sums (combination method). The problem of constructing a systematically statistical theory of ion hydration (solvation) in solution is discussed.

In the current theory of electrolyte solutions we can distinguish two fundamentally different approaches to the question of the model of the electrolyte solution: we have a model involving spatially distributed particles, in which the particles of solvent and electrolyte are regarded as equals (discrete solvent model), and a continuous model, in which the solvent is regarded as some kind of field and is taken into account by introducing the dielectric constant ϵ into the expression for the interaction between the ions.

The first model, which was first discussed in [1, 2] and then in [3] and was then considerably developed in [4, 5], et al., is undoubtedly the more physically realistic. In principle, it makes it possible (with systematic allowance for the interaction between "sufficiently large" groups of particles) to describe the solvation of ions in solutions, the formation or destruction of the structure of a solution, the formation of ion pairs, etc. The computation problems increase very severely, however, when allowance is made for ever increasing numbers of interacting particles. In essence, this corresponds to the problems arising in attempts to create a systematic theory of the liquid state.

The second model, although physically less realistic, gives a fairly good description (when the potential of the short-range interaction between the ions is used in arbitrary form) of the thermodynamic and thermochemical properties of solutions of strong electrolytes over a certain range of electrolyte concentrations and provides qualitative and semiquantitative information about the structure of the solution, the solvation of ions in solutions and other effects (see [6] for a review of these works).

In the present work, we will discuss the concept of a structural solvent in the statistical mechanics of electrolyte solutions, proceeding from the outset from a given arbitrary form of the binary interaction potential both between the ions and between the ions and solvent molecules. The results may represent the basis of a systematically statistical theory of ion hydration (solvation) in electrolyte solutions if we start from concrete forms of the ion-molecule interaction obtained on the basis of electrostatic and quantum-mechanical calculations (ion-dipole, ion-quadrupole, etc., interactions, induction and dispersion interactions, and repulsive forces).

The present method of allowing for the discrete structure of the solvent in the theory of statistical equilibrium of mixed systems is based on a general analysis of the configuration integral of the whole system (solvent+solute) and the representation of the term involving the interaction energy of the two subsystems in the configuration integral by means of Maier sums (combination method).

For this purpose, let us consider an initial system of N solvent molecules and n solute ions occupying a volume V . Furthermore, let $U_N(R_1, \dots, R_N)$ be the potential energy of only the subsystem of N solvent

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