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TEMPERATURE BEHAVIOR OF THE ADSORPTION OF INTERACTING PARTICLES

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The study of the adsorption of particles from the gas phase and from their solutions has a long history. To describe the adsorption a considerable number of different isotherms have been proposed which are built upon certain models with respect to the properties of the surface and of the adsorbing particles, and which also adopt simplifications of a mathematical nature [1-7]. Allowance for the interaction of the adsorbed particles between themselves which leads to qualitatively new effects was first made by Frumkin [8] for the Langmuir isotherm. Later interaction was taken into account in a similar way for a number of other, more complicated isotherms [9-11]. It was found that attractive interaction between the adsorbed particles can lead to a discontinuous change in the degree of coverage, θ ($0 \leq \theta \leq 1$), as function of the concentration (or pressure) of the adsorbing particles in the solution (or gas). A number of highly significant features are also uncovered when examining the temperature dependence of θ . It is the purpose of the present communication to present the results of an analysis of the temperature behavior of an adsorption system of particles interacting on the surface.

Let us examine a system where the adsorption isotherm is described by the relation*

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

Here $m > 1$ is the number of adsorption sites occupied on the surface by one adsorbed particle, c is the concentration of particles in the bulk of the solution, $a > 0$ is the attraction constant describing the interaction between the adsorbed particles, and $B = \chi \exp(-w/kT)$, where $w \geq 0$ is the energy change of the particles during adsorption and χ is a constant not depending on θ or c which is related to the entropy change of the particles during adsorption; quantity a can be written as $a = \lambda/kT$ where $\lambda > 0$ is independent of temperature. In the case $m = 1$, Eq. (1) becomes the Frumkin isotherm [8]

$$\theta/(1-\theta) = Bc \exp(a\theta). \quad (2)$$

For the sake of definition, systems will be analyzed below which are described by isotherms (1) and (2), but the principal results can be transferred to an extremely broad class of adsorption systems with interaction between the particles.

When quantity a is sufficiently large, the θ - c relation defined by isotherms (1) and (2) will have an S-shaped section (cf. Fig. 1). As a result, quantity θ increases monotonically with c , undergoes a discontinuous change at $c = c_{cr}$, and then $\theta(c)$ again increases monotonically. The value of c_{cr} is determined by the "area rule" which effectively corresponds to equality of the free energies of the system before and after the discontinuity in θ (Fig. 1). The free energy, F , of a system according to (1) and (2) can be obtained, in particular, by use of the average-field approximation for the energy of interaction and of the methods of the theory of combinations in calculating the configurational entropy:

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

*Isotherm (1) often is called the Flory-Huggins isotherm, since it can be obtained from a lattice model similar to that used by these authors in describing the properties of polymer chains in solution [12, 13].

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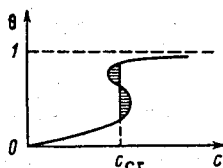


Fig. 1

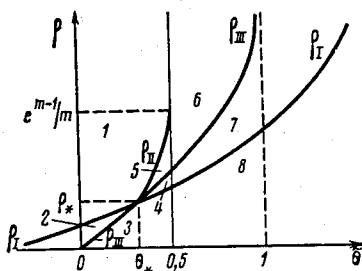


Fig. 3

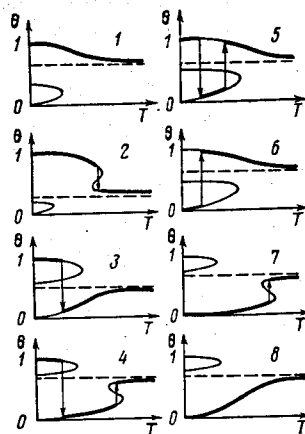


Fig. 2

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

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

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

where $\rho \equiv \chi c$, c here being 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 (3) from the condition $\partial F / \partial \theta = 0$, 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 determine the temperature behavior of the system. Similar relations have been examined in [14] when analyzing phase transitions in asymmetric systems becoming disordered.

Over certain ranges of parameters ρ and $\tilde{\theta}$, Eq. (4) at some T has only one solution, at others it has three ($0 \leq \theta_1 \leq \theta_2 \leq \theta_3 \leq 1$) (cf. Fig. 2). The smallest, θ_1 , and the largest, θ_3 , of the roots of Eq. (4) correspond to minima, the intermediate root θ_2 corresponds to a maximum of $F(\theta)$. The system will be in that state among the two states θ_1 and θ_3 which corresponds to the absolute minimum of $F(\theta)$. Under the condition $F(\theta_1) = F(\theta_3)$, discontinuous transitions $\theta_1 \rightarrow \theta_3$ or $\theta_3 \rightarrow \theta_1$ are realized. Substitution of the values $\theta_{1,3}(T, \tilde{\theta}, \rho, \lambda, m)$ into the equality $F(\theta_1) = F$ defines the temperature of the discontinuous transition.

If the parameter ρ equals some critical value $\rho = \rho_I$ (which depends on $\tilde{\theta}$ and m), then the three solutions merge into one: $\theta_1 = \theta_2 = \theta_3 = \theta_*$, where $\theta_* = 1/(1 + \sqrt{m})$; here the equation $\partial^2 F / \partial \theta^2 = 0$ has a single root, and the quantity $\lambda/kT = \xi = (1 + \sqrt{m})^2$. This situation corresponds to the development or disappearance of an S-shaped section on the curve $\theta(T)$ which is the solution of Eq. (4): cf. Fig. 2, cases 2, 4, and 7 (we note that the development of an S-shaped section on the curve of the $\theta(c)$ dependence [cf. Fig. 1] corresponds to the same value $\theta = \theta_* = (1 + \sqrt{m})^{-1}$ [7]).

The examination shows that the critical value $\rho = \rho_I$ is given by the relation

$$\rho_I = \rho \cdot \exp[\xi(\tilde{\theta} - \theta_*)], \quad (5)$$

where $\rho_* = \theta_*/m(1 - \theta_*)m$. In the plane of the parameters (cf. Fig. 3), the critical curve 5 corresponds to the development or disappearance of one transition in the system. It turns out, in addition, that at certain values of the parameters $\tilde{\theta}$ and ρ for $m > 1$, a pair of transitions can be realized in the system with changing temperature

(Fig. 2, part 5). The corresponding critical curve ρ_{II} (cf. Fig. 3) corresponding to the development (disappearance) of a pair of transitions unites the points $(\tilde{\theta} = \theta_*, \rho = \rho_*)$ and $(\tilde{\theta} = 1/2, \rho = e^{m-1/m})$. Near the point $(1/2, e^{m-1/m})$ a second critical curve is given by the expression[†]

$$\tilde{\theta} - 1/2 = [m - 1 - \ln(m\rho_{II})] / 2m \ln[m - 1 - \ln(m\rho_{II})]. \quad (6)$$

The transitions in the system can be of two types: 1) solutions of Eq. (4) (or (1)) for $T \rightarrow \infty$ not attended by a discontinuous transition across the asymptote of θ_∞ , i.e., $\theta_\infty/m(1 - \theta_\infty)^m = \rho$ (cf. Fig. 2, parts 2, 4, and 7), and 2) solutions attended by such a discontinuous transition, i.e., supertransitions (cf. Fig. 2, parts 3-6). The curve $\rho_{III}(\tilde{\theta})$ defined by the equation

$$\rho_{III} = \tilde{\theta}/m(1 + \tilde{\theta})^m, \quad (7)$$

separates the plane of the parameters $(\tilde{\theta}, \rho)$ into two regions corresponding to the above two types of transition.

The vertical line $\tilde{\theta} = 1/2$ divides the plane $(\tilde{\theta}, \rho)$ into two regions corresponding to two essentially different starting states of the system. It follows from (3) that at $\tilde{\theta} > 1/2$ and $T \rightarrow 0$ we have $F(0) < F(1)$ so that the system is in state θ_1 , while at $\tilde{\theta} < 1/2$ and $T \rightarrow 0$ we have $F(0) > F(1)$ and the system is in the state θ_3 .

Thus, the plane of the parameters $(\tilde{\theta}, \rho)$ proves to be divided into 8 regions. The examination shows that in region 1 there are no transitions associated with a discontinuous change of θ with temperature, whereas in regions 2 and 3 only one transition $\theta_3 \rightarrow \theta_1$ is realized; in region 3 this is a supertransition. The specific properties of systems described by isotherm (1) ($m > 1$), in contrast to the case of $m = 1$ which corresponds to isotherm (2), are displayed in regions 4 and 5. Region 4 is reached from region 3 by crossing of the curve $\rho_I(\tilde{\theta})$, whereupon a transition arises in the system in the S-shaped section of the $\theta(T)$ dependence (Fig. 2, case 4). If the transition on the left-hand side satisfies the condition $\theta_1 \ll 1, 1 - \theta_3 \ll 1$ ("strong" transition), and that on the right-hand side satisfies the condition $\theta_3 - \theta_1 \ll 1$ ("weak" transition), then the corresponding transition temperatures which can be found from (3) and (4) are given by

$$kT^{(s)} = \frac{\lambda(1/2 - \tilde{\theta})}{\ln(m\rho) - m + 1}, \quad kT^{(w)} = \frac{\lambda(\tilde{\theta} - \theta_*)}{\ln(\rho/\rho_*)}. \quad (8)$$

Passing from region 1 into region 5 we cross the critical curve ρ_I . This was pointed out above to be attended by the development of two supertransitions in the system. When both of these supertransitions are strong, then the temperatures of the left-hand and right-hand transition are given by

$$kT^{(s,l)} = \frac{\lambda(1/2 - \tilde{\theta})}{\ln(m\rho) - m + 1}, \quad kT^{(s,r)} = \frac{\lambda(\tilde{\theta} - 1)/2}{\ln\{m\rho[m - 1 - \ln(m\rho)]^m\}}. \quad (9)$$

At $\theta > 1/2$ where the starting state is $\theta_1 = 0$, the situation is as follows. In region 6 there is one supertransition ($\theta_1 \rightarrow \theta_3$); in region 7 there is one transition analogous to the right-hand transition in region 4. In region 8 there are no transitions. We also point out that expressions (8) give the temperatures of the "strong" and "weak" transition, not only in region 4 but also when only one transition is realized (regions 2, 3, 6, and 7).

Let us formulate, in conclusion, the special features of the temperature behavior of adsorption systems with interaction between the adsorbed particles which have been established above. We note in doing so that although for the sake of definition the isotherms (1) and (2) have been analyzed in the present work, it can be shown that the results obtained are of a more general character. By comparing Figs. 1 and 2 one can see that the temperature behavior $\theta(T)$ has much more interesting and diverse possibilities than the behavior of $\theta(c)$. A qualitatively new aspect is the possibility that supertransitions are realized here, so that different sections of the $\theta(T)$ dependence are located to different sides of the asymptote of θ_∞ . Double transitions also can be realized in the system: With increasing temperature there is sudden desorption, and then, at some higher temperature, there is sudden adsorption. This last effect which is associated with the realization of double transitions can only develop in asymmetric systems. It occurs in particular for isotherm (1), the range of the double transitions being wider the higher m . For isotherm (2) (symmetric system), $\theta_* = 1/2$, the interval $[\theta_*, 1/2]$ contracts to a point, and double transitions are absent.

[†]The equation of the second critical curve is obtained from the condition that functions $F(T, \theta_1(T))$ and $F(T, \theta_3(T))$ not only have a common point but are tangent in this point [14].

It is important to note that during adsorption studies in electrochemical systems one has the possibility by varying the concentration of the adsorbing particles and the electrode potential to control the parameters of the system, and thus realize conditions under which the predicted effects will show up.

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SOLVENT EFFECTS ON THE THERMAL *cis,trans* ISOMERIZATION OF SUBSTITUTED AZOBENZENES

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Correlation equations have become widely used in theoretical organic chemistry [1]. However they are far from invariably able to provide a quantitative or even a semiquantitative indication of the reactivity of organic compounds. The proliferation of γ substituent constants has led to their being preferred for correlation, but it is the empirical nature of the quantities σ and ρ that constitutes the defect inherent in the Jaffé, Hammett, and Taft equations. But for processes that proceed via a triplet state intermediate or involve free radicals, the absence of similar correlations is generally typical. This demonstrates that the whole diverse range of chemical and biochemical reactions and the data from the study of these processes and of organic molecules by physical methods cannot be reduced to polar effects with the exclusion of exchange interactions. Only when the polar effect predominates would we expect to encounter Hammett or similar correlations. And conversely, when exchange interactions dominate in a homologous series an alternating effect often appears. We have demonstrated this as exemplified by the thermal *cis,trans* isomerization of mono- and disubstituted azobenzenes, which is thought to proceed via the triplet state.

The solvation properties of the solvent have a considerable effect on the rate of this reaction.

Many solvates, complexes, and weak associates can be stabilized by exchange or by polar interactions [3]. The absence of both an alternating and a Hammett correlation demonstrates that the contributions of

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