

Description of the anomalous features in nonequilibrium processes on solid surfaces near a second-order magnetic phase transition

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A description based on the fluctuational theory of phase transitions and a random-walk model is proposed for the anomalous features in activated surface processes near a volume magnetic phase transition. Experimental results on the change in the rate of the initial oxidation of iron near the Curie point T_C are explained for the first time.

Research on several activated processes, such as chemical reactions,¹ desorption,² and sublimation,³ on the surfaces of solids, in which a second-order volume magnetic phase transition occurs as the temperature changes, has revealed characteristic deviations of the rate (k) of the process from the Arrhenius law $k = k_0 \exp(-E_a/T)$ (E_a is the activation energy of the process) near the transition point. It has been found that there is a turning point at $T = T_C$, that there are extrema before or after the transition point, and that the activation energies differ on the two sides of the transition point.

In this letter we offer an approach for describing such processes. As an example, we describe the behavior of the rate of the initial oxidation of iron to FeO. Experimentally, the limiting step is the chemical reaction itself.¹ Previous attempts to derive a corresponding theory⁴ have not succeeded in reaching agreement with experiment. To describe this chemical reaction we assume that the oxygen atoms on the surface do not interact with each other and that the behavior of the solid (iron) near the transition point can be described by the fluctuational theory of equilibrium phase transitions in an unbounded medium.⁵ Recent research has shown that a chemisorbed particle on the surface of a magnetic material is in a spin-polarized state.⁶

We will therefore assume that the exchange part of the interaction of the O atom with the solid is determined by the intrinsic spin of the particle, \hat{S} . It is then sufficient to examine the behavior of a single O atom on the solid surface; this atom is being acted upon by random forces due to fluctuations in the solid. In the random-walk

theory, a chemical reaction is a process by which a particle escapes from a deep potential well (the depth of the well, V_B , is equal to the activation energy, and we have $V_B/T > 1$). In this case the reaction rate is determined by the ratio of the flux density of particles out of the well, j_B , to the total number of particles in the well, n_A . We approximate the actual three-dimensional motion of the O atom in the course of the reaction as a one-dimensional motion along the so-called reaction coordinate q . The distribution function $\rho(p, q, t)$ of oxygen atoms, which we will need in order to determine j_B and n_A , obeys the Fokker-Planck equation

$$\frac{\partial \rho}{\partial t} + \frac{p}{M} \frac{\partial \rho}{\partial q} + K(q) \frac{\partial \rho}{\partial p} = \eta \frac{\partial}{\partial p} \left(p \rho + MT \frac{\partial \rho}{\partial p} \right), \quad (1)$$

where M and p are the mass and momentum of the particle, and $K(q)$ is a regular force exerted on the particle. The coefficient of friction, η , expressed in terms of the correlation function of the random forces acting on the particle, can be written⁷

$$\eta = \frac{1}{MT} \lim_{\omega \rightarrow 0} \operatorname{Re} \int_0^{\infty} e^{i\omega\tau} \langle \hat{\mathcal{F}}_0^* \hat{\mathcal{F}}_0(\tau) \rangle d\tau, \quad (2)$$

where $\hat{\mathcal{F}}_0 = \hat{F} - \langle \hat{F} \rangle$, $\hat{F} = -(\partial \hat{H} / \partial q)$, \hat{H} is the Hamiltonian of the system, and the angle brackets denote the expectation value over the heat reservoir (the solid). Kramers⁸ has derived the following solutions of Eq. (1) for the cases of weak, strong, and intermediate friction forces, respectively:

$$k = \begin{cases} \eta \frac{V_B}{T} \exp(-V_B/T), & \eta < \omega_A \frac{T}{V_B}, \end{cases} \quad (3a)$$

$$k = \begin{cases} \omega_A \exp(-V_B/T), & \omega_A \frac{T}{V_B} < \eta < \omega_B, \end{cases} \quad (3b)$$

$$k = \begin{cases} \frac{2\pi\omega_A\omega_B}{\eta} \exp(-V_B/T), & \eta > \omega_B, \end{cases} \quad (3c)$$

$$V_B = F_B - F_A, \quad F_{A(B)} = F_{A(B)}^0 + F_{A(B)}^{\text{sp}}, \quad (4)$$

where $F_{A(B)}^{\text{sp}}$ and $F_{A(B)}^0$ are the parts of the free energy F which respectively do and do not depend on the exchange interaction of the O atom with the solid, and $\omega_{A(B)}^2 = (1/M) |(\partial^2 F / \partial q^2)|_{A(B)}$. The meaning of the points A and B is clear from Fig. 1. We see from (3) that in order to determine k we need to calculate η and V_B , taking into account the exchange interaction of the O atoms with the semi-infinite solid. Since the renormalization-group method has not yet been applied to the description of phase transitions in semi-infinite media,⁵ we will use a simple Gaussian approximation⁹ to derive analytic expressions for η and V_B . As is shown below, this approach is successful in explaining the experimental data available. We write F^{sp} as

$$F_{A(B)}^{\text{sp}}(\mathbf{R}) = \langle \int d\mathbf{r} J(|\mathbf{R}_{A(B)} - \mathbf{r}|) \hat{\mathbf{S}} \cdot \hat{\mathbf{S}}(\mathbf{r}) \rangle, \quad (5)$$

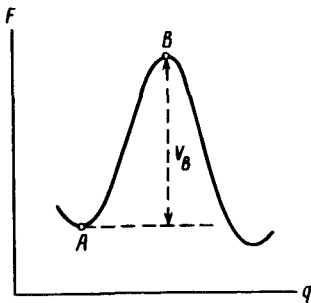


FIG. 1.

where R is the radius vector of the particle, $\hat{s}(\mathbf{r})$ is the spin of the component, $J(|\mathbf{R} - \mathbf{r}|)$ is the exchange integral, and the integration in (5) is carried out over the volume of the solid. We can find

$$V_B = Q + \langle \int \{ J(|\mathbf{R}_B - \mathbf{r}|) - J(|\mathbf{R}_A - \mathbf{r}|) \} \hat{\mathbf{s}} \cdot \hat{\mathbf{s}}(\mathbf{r}) d\mathbf{r} \rangle, \quad (6)$$

where $Q = F_B^0 - F_A^0$. To evaluate the integral in (6) we choose the Hamiltonian of the magnetic material in Landau-Ginzburg form:

$$\hat{H}_{\text{solid}} = \int d\mathbf{r} [a_0 + a_2 \hat{\mathbf{s}}^2 + a_4 \hat{\mathbf{s}}^4 + c(\nabla \hat{\mathbf{s}})^2]. \quad (7)$$

We then have

$$\langle \hat{s}_z(\mathbf{r}) \rangle = \begin{cases} 0, & T > T_C \\ \sqrt{|a_2|/2a_4}, & T < T_C \end{cases} \quad (8)$$

The reaction barrier V_B is given by

$$V_B/T = (Q/T_C)x + \alpha \sqrt{(x^2 - x)\Theta(x - 1)}, \quad (9)$$

where $x = T_C/T$, $\alpha = (J(0)Sf/\pi T_C)\sqrt{a_2' T_C/2a_4}$, $\Theta(x - 1)$ — is the unit step function, the number f depends on $|\mathbf{R}_B - \mathbf{R}_A|$, and $J(0)$ is the Fourier transform of $J(|\mathbf{R} - \mathbf{r}|)$ at $\mathbf{k} = 0$. In the expression for η we consider only the correlations of the fluctuations of the spin density of the solid. In this case we have

$$\eta = \frac{S(S+1)}{(2\pi)^2} \frac{cJ^2(0)\Lambda^3}{MT_c} x \begin{cases} \frac{1}{3} - b \frac{1-x}{x} + \left(\sqrt{b \frac{1-x}{x}} \right)^3 \arctan \sqrt{\frac{x}{b(1-x)}}, & x \leq 1, \\ \frac{1}{3} - 2b \frac{x-1}{x} + \left(\sqrt{2b \frac{x-1}{x}} \right)^3 \arctan \sqrt{\frac{x}{2b(x-1)}}, & x > 1, \end{cases} \quad (10)$$

where $b = a_2' T_C/cA^2$, and A is a cutoff parameter.

Figure 2 shows the T dependence of the reaction rate found from (3), (6), and (10). We see from Fig. 2 that these expressions describe all the experimental characteristics

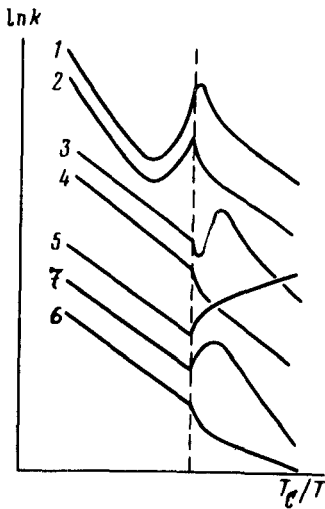


FIG. 2. Weak friction: 1— $\alpha < 0.2$; 2— $\alpha > 0$. Strong friction: 3— $3 - 1/2b - Q/2bT_c > 0$; 4— $3 - 1/2b - Q/2bT_c < 0$. Intermediate friction: 5— $\alpha < 0$, $Q/T_c < |\alpha|$; 7— $\alpha < 0$, $Q/T_c > |\alpha|$.

listed above. The extremum in the region $0 < x \leq 1$ is found only in the case of a weak frictional force.

Figure 3 compares the experimental results on the initial oxidation of iron¹ with the theoretical results. The theoretical curve with the parameter values $Q/T_c = 31.03$, $b = 37.96$, and $\alpha = -12.39$ agrees with the experimental data (the points) within the experimental error.

The experimental values of the critical indices determining the temperature dependence of the correlation function and of the order parameter for iron are known⁹ to be $\eta_{\text{expt}} = 0.07 \pm 0.07$ and $\beta = 0.34 \pm 0.02$. These values differ from the critical indices in the Gaussian approximation. It is surprising to find that the experimental data can be described successfully in the Gaussian approximation. Further calculations show that the use of the experimental values of the indices degrades the agreement between the values found here for the oxidation rate and the experimental values. We

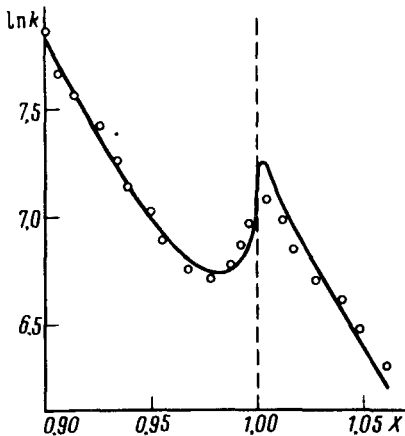


FIG. 3.

believe that further study is required to determine how the surface affects the phase transition.

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¹G. C. Measor and K. K. Afzulpurkar, *Philos. Mag.* **10**, 817 (1964).

²M. R. Shanabarger, *Phys. Rev. Lett.* **43**, 1964 (1979).

³B. S. Sales, D. E. Turner, and M. B. Maple, *Phys. Rev. Lett.* **44**, 586 (1980).

⁴H. Suhl, in: *The Physical Basis for Heterogeneous Catalysis* (ed. E. Drauhlis and R. I. Jaffee), New York, 1975, p. 427.

⁵A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, *Fluktuatsionnaya teoriya fazovykh perekhodov* (Fluctuational Theory of Phase Transitions), Moscow, 1982.

⁶G. L. Mórán-López and L. M. Falicov, *Phys. Rev.* **B26**, 2560 (1982).

⁷N. L. d'Agliano *et al.*, in: *Nobel Symposium 24, Collective Properties of Physical Systems* (ed. B. Lundqvist and S. Lundqvist), New York, 1974, p. 200.

⁸H. A. Kramers, *Physica (Utrecht)* **7**, 284 (1940).

⁹S. Ma, *Critical Phenomena*, Benjamin, New York, 1976 (Russ. transl. Moscow, 1980).

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