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SOME SPECIAL FEATURES OF THE LE CHATELIER–BRAUN PRINCIPLE

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The relaxation reaction of a system that follows from the Le Chatelier–Braun principle and weakens the result of an external influence turns out to be more intense under a complex action. A method for quantitative determination of the weakening effect for simple and complex actions is suggested.

The thermodynamic principle formulated at the end of the last century by Le Chatelier and Braun reads: an external action disturbing a system from an equilibrium state produces in it processes that weaken the results of this action. The indicated principle is a universal law of nature that the trend in allows one to predict the direction of the thermodynamic processes appearing in a system under an external action.

Nevertheless, being the result of generalization of numerous experimental facts, the Le Chatelier–Braun principle has not received wide application in thermodynamics. In our opinion, the reasons for this are as follows: in the formulation of the principle, conditions for its applicability are absent; the qualitative character of the principle does not enable one to reveal the mechanism and degree of weakening of the external action on the system; the interpretation of the principle that mixes relaxation reactions that are dissimilar in nature and appear in the thermodynamic system under various external actions is too general.

Below we present results of analyzing the problem that has arisen that will help in the practical application of the Le Chatelier–Braun principle in investigating various thermodynamic processes.

1. The Le Chatelier–Braun principle is applicable not to every external action on an arbitrary equilibrium system. The conditions for the applicability of this principle are as follows: a thermodynamic system subjected to an action must at the initial instant of time be in a stable-equilibrium state and the intensity of the external action must not exceed the limiting value at which this system is destroyed.

2. For a quantitative characteristic of the degree of weakening of an external action on a system we suggest introducing a coefficient δ that is equal to the ratio of the magnitudes of the basic change, under the external action, in a thermodynamic parameter of the system in the final and initial states. Thus, for example, with increase in the external pressure on a body at equilibrium its volume will decrease from the initial V to a certain V^* at which the pressure p_{i}, increasing inside the body, becomes equal to the action pressure p_{e} and equilibrium occurs in the system again, i.e.,

$$\delta = \frac{V^*}{V_0} . \tag{1}$$

From general physical considerations it is clear that the value of the indicated weakening coefficient depends on both the type of body subjected to the action and the character of the external process accomplishing this action.

3. The relaxation reactions appearing in bodies under an external action exerted on them can be divided into two types, namely, simple and complex, which differ in the degree of change of the independent thermodynamic parameters and weaken to a different extent the result of the action exerted on the body.

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We call an external action and the relaxation reaction produced by it simple if in the system only one parameter, namely, the corresponding (direct) parameter, is changed. But if in the system an action produced a relaxation reaction in which changes occur not only in the direct thermodynamic parameter but also in the indirect independent variables of the system, the processes of the action and the relaxation are complex. In this case the changes in each independent parameter of the system occur toward a counteraction to the external perturbation. Put together, these counteractions increase the weakening coefficient δ compared to the case of a simple action.

Let us give examples that illustrate the expendiency of the statements presented above.

Example 1. Suppose the system is a gas in a cylinder with a piston and its independent parameters are the volume V and the temperature T; they correspond to generalized forces, namely, the pressure p and the entropy S. At the initial instant the gas volume is equal to V_{0i} and the internal pressure p_{0i} is equal to the external p_{0e}. We begin to increase quasistatically (isothermally) the external pressure to a certain value p_e^*. Under this action the direct parameter, namely, the gas volume V, will decrease, while the indirect parameter, namely, the temperature T, remains constant. It is clear that here the action and the relaxation reaction produced are simple.

In the course of the process under consideration the internal pressure p_i will increase, exerting resistance to the gas compression and weakening the result of the external action. This situation continues until the gas volume reaches V^*, at which the gas pressure p_i turns out to be equal to p_e^*, and equilibrium will be established again in the system.

We determine the value of the isothermal weakening coefficient in this simple process. According to Eq. (1), $\delta_T = V^*/V_0$; assuming that the gas is ideal and obeys Mariotte's law $p_0V_0 = p^*V^*$, we have

$$\delta_T = \frac{p_{0i}}{p_i^*}.$$

Taking into account, now, that in the initial and final equilibrium states the internal and external actions are equal, we finally obtain

$$\delta_T = \frac{p_{0e}}{p_e^*}. \tag{2}$$

We consider the case of a complex action on the system. When the external pressure increases very rapidly, the compression of the gas occurs adiabatically, i.e., along with a decrease in the volume V we observe an increase in the temperature T of the gas. In this process the relaxation reaction is complex. We determine what the isentropic weakening coefficient δ_S is equal to in this case. Since the increase in the gas temperature leads to an additional increase in the internal pressure, already from qualitative considerations it is clear that $\delta_S > \delta_T$.

Indeed, in adiabatic compression the gas obeys Poisson's law

$$p_{0i}V_0 = p_i^*(V^*)^\gamma, \quad \text{where } \gamma = C_p/C_V.$$

Calculating the value of the isentropic coefficient $\delta_S = V^*/V$, with account for the equalities $p_{0i} = p_{0e}$ and $p_i^* = p_e^*$ we obtain the relation

$$\delta_S = \sqrt[\gamma]{\left(\frac{p_{0e}}{p_e^*}\right)}. \tag{3}$$

Hence it follows that

$$\delta_S = \sqrt[\gamma]{\delta_T}\,. \tag{4}$$

Since $\gamma > 1$ and the ratio p_{0e}/p_e^* is less than unity, we conclude that the weakening coefficient for the result of the external action in the complex (adiabatic) process is larger than that in the simple (isothermal) process

$$\delta_S > \delta_T\,. \tag{5}$$

Example 2. Let us consider a case of application of the Le Chatelier–Braun principle to electrodynamics. As the thermodynamic system, we select an isotropic dielectric in an external electric field **E**. As the independent parameters, we take the temperature T and the induction **D**, assuming that the body volume remains constant. In polarization of the dielectric we observe an electrocaloric effect, i.e., heating of the dielectric. According to the Le Chatelier–Braun principle, an increase in the dielectric temperature is accompanied by the opposite effect, namely, by a decrease in its polarization. A simple action can be accomplished by placing the dielectric between the plates of a capacitor whose charge remains constant (and hence **D** = const). Here one independent parameter T changes.

A complex action can be performed by placing the dielectric in a capacitor that is connected to a current source. The field intensity **E** remains constant, while both independent parameters **D** and T vary, thus enhancing processes that weaken the result of the external action. Mathematically, this situation is described by the inequality

$$C_E > C_D > 0\,.$$

We will show this. The free energy F will be the basic thermodynamic potential that corresponds to the given set of independent parameters. For a fixed number of particles and at a constant volume we can write for the free energy F:

$$dF = -S dT - \frac{1}{4\pi}\mathbf{E}\,d\mathbf{D}\,. \tag{6}$$

In this case the adiabaticity condition and Maxwell's thermodynamic equality will be written, respectively, in the form

$$dS = \left(\frac{\partial S}{\partial T}\right)_D dT + \left(\frac{\partial S}{\partial \mathbf{D}}\right)_T d\mathbf{D} = 0 \quad \text{and} \quad -4\pi\left(\frac{\partial S}{\partial \mathbf{D}}\right)_T = \left(\frac{\partial E}{\partial T}\right)_D . \tag{7}$$

Taking into account that $C_D = T\left(\frac{\partial S}{\partial T}\right)_D$, from Eq. (7) we have

$$C_D \frac{dT}{T} - \frac{1}{4\pi}\left(\frac{\partial \mathbf{E}}{\partial T}\right)_D d\mathbf{D} = 0\,. \tag{8}$$

As the independent variable, we select **E** instead of **D** and obtain in a similar way

$$C_E \frac{dT}{T} + \frac{1}{4\pi}\left(\frac{\partial \mathbf{D}}{\partial T}\right)_E d\mathbf{E} = 0\,. \tag{9}$$

From relations (8) and (9) it is possible to find the difference in the heat capacities in the form

$$C_E - C_D = -\frac{T}{4\pi}\left(\frac{\partial \mathbf{D}}{\partial T}\right)_E \left(\frac{\partial \mathbf{E}}{\partial T}\right)_D .$$

As expected, the difference turns out to be positive, since $\left(\frac{\partial \mathbf{D}}{\partial T}\right)_E < 0$, which implies a decrease in the polarization of the dielectric with increase in its temperature in a constant electric field.

CONCLUSIONS

1. A quantitative measure of the weakening reaction of a system can be the ratio of the values of a thermodynamic parameter subjected to the action in the initial and final equilibrium states.

2. There are two types of external actions on an equilibrium thermodynamic system, namely, simple and complex. The weakening coefficient for the result of the action in the case of a complex relaxation reaction is always larger than that in the case of a simple reaction.

NOTATION

T, temperature; V, volume; S, entropy; F, free energy; C, heat capacity; p_i and p_e, internal and external pressure; δ, weakening coefficient for the action; γ, adiabatic exponent; $\mathbf{E}$ and $\mathbf{D}(E, D)$, intensity and induction of the electric field. Subscripts: i and e refer to the internal and external parameters, respectively; S, T, E, D, p, and V indicate which parameters remain constant; 0 and * refer to the initial and final equilibrium states.