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Thermodynamic aspects of materials science

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As materials science studies physicochemical properties of materials, it needs a support of thermodynamics, which predicts general regularities for physicochemical properties of matter. This survey deals with solid materials the thermodynamic description of which is especially complicated. The achievements of last years provide better insight in the chemical potential anisotropy and, on this grounding, in the anisotropy of chemical affinity governing all processes in solid materials. The survey summarizes novel approaches and thermodynamic equations and then exhibits their use in materials science. As examples, the solubility, creep and corrosion of materials are analyzed. A newly discovered phenomenon, the strain sign effect in corrosion under stress (*e.g.*, a difference in the corrosion rate on the opposite sides of a bent metallic plate), is described and explained thermodynamically. A modern theory of the strength of materials developed during last years is also presented with the characterization of crack properties, the mechanisms of crack propagation and estimation of the ultimate stress. The development of this area required the introduction of a novel thermodynamic potential that formed the basis for the theory of strength.
The bibliography includes 47 references.

Contents

I.	Introduction	1
II.	Anisotropy of chemical potential	2
III.	Chemical affinity tensor	4
IV.	Creep of materials	5
V.	Corrosion of materials. Role of surface	6
VI.	Strength of materials	9
VII.	Conclusion	13

I. Introduction

As a department of knowledge related to materials, modern materials science is of top-priority applied significance and seems simply to serve practical needs. What kind of science can be discussed here and does materials science as a whole refer to technology? As is known, the subject of technology is a fabric or product, whereas the subject of science is a phenomenon. Let us take graphene, the most famous today's material, as an example. Of course, graphene itself is a product out of which many other things can be fabricated. However, that fact that graphene is a two-dimensional solid without an energy gap is certainly a phenomenon. One can say the same about any other property. Obviously, the manifestation of properties by a body is worthy of scientific study. Therefore, it is not surprising that materials science is often defined as a science studying physicochemical properties of materials. But what is a material? Even the natural-scientific understanding of this term is conditional, not speaking about its multiple meanings in various fields of human activity. In the author guide, the journal '*Nature Materials*' defines materials 'as substances in the condensed states (liquid, solid, colloidal) designed or manipulated for technological ends'. Using such utilitarian approach, any body needed for technology is declared to be a material and others to be not. However, science studies objects irrespective of whether they are needed or not to someone. Then it follows that materials science as a pure science is faceless. But the face is resumed when science is combined with technology. So the standard term '*Materials Science & Engineering*' more exactly mirrors the meaning of the term 'materials science'. Its technological component is principal, and every material scientist is a chemical engineer first of all. In his/her activity, a materials scientist deals with various sciences. The goal of this survey is demonstrating what thermodynamics has made and yields for materials science.

Naturally, we focus on chemical thermodynamics rather than thermodynamics in general. Gibbs is rightly considered to be the father of chemical thermodynamics because he

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introduced the concept of chemical potential, a principal characteristic of matter and, hence, of any material. On the ground of chemical potential, there is constructed chemical affinity determining the direction and rate of all physicochemical processes (including chemical reactions). Great mission of thermodynamics is relating the chemical potential to the properties of matter. For instance, thermodynamics creates thermochemistry by coupling the chemical potential and temperature, mechanochemistry by coupling the chemical potential and stresses, electrochemistry by coupling the chemical potential and electric potential, and surface science by coupling the chemical potential and surface tension, *etc*. We can illustrate this relation by writing a simple fundamental equation for the free energy, F, of a homogeneous system

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \sum_k X_k \mathrm{d}x_k + \sum_i \mu_i \mathrm{d}N_i \qquad (1)$$

where S is entropy, T is temperature, p is pressure, V is volume, X_k and x_k are the strength of an external field of kind k and a corresponding polarization, μ_i is the chemical potential and N_i is the number of particles of component i, respectively. At a proper choice of components as independent substances or their combinations, Eqn (1) is the total differential of free energy. For this reason, the reciprocity relations follow

$$\frac{\partial \mu_i}{\partial T} = -\frac{\partial S}{\partial N_i}, \quad \frac{\partial \mu_i}{\partial V} = -\frac{\partial p}{\partial N_i}, \quad \frac{\partial \mu_i}{\partial x_k} = \frac{\partial X_k}{\partial N_i}$$

leading to the above interrelations between the chemical potential and the properties of a system. Eqn (1) also establishes the interrelations between other parameters of the system:

$$\frac{\partial p}{\partial T} = \frac{\partial S}{\partial V}, \quad \frac{\partial X_k}{\partial T} = -\frac{\partial S}{\partial x_k}, \quad \frac{\partial X_k}{\partial V} = -\frac{\partial p}{\partial x_k}$$

By writing the fundamental equations for other thermodynamic potentials, we can obtain a lot of similar relationships for various variables. Among them, we always can choose most convenient relationships for solving this or that problem. Thus, thermodynamics can be useful for materials science in that respect that makes possible calculating a given property *via* another property without resorting to an additional experiment.

The above example of a fundamental equation refers to a fluid. Fundamental equations for solids are more complicated, and reciprocity relations are more numerous. However, this does not change the core of the subject, and the foregoing holds in any case. As the main kind of a material, a solid deserves detailed consideration, and we will address a solid material in this paper.

II. Anisotropy of chemical potential

A distinguishing feature of a solid is its ability to respond to a change in the shape. Continuum mechanics assumes every solid to possess a certain configuration (termed as an undistorted configuration) a non-orthogonal deformation of which is detectable using some subsequent experiment (see p. 191 in Ref. 1).This configuration is a stable (at least, within a certain timeslot) distribution of particles in space, which is termed a lattice. A regular lattice corresponds to a crystalline state. An irregular lattice corresponds to an amorphous state (although amorphous, for example, glassy state can be transitional with respect to a solid state on the scale of large times, it shows all the signs of a solid-like behaviour). The limiting case of a true solid material is perfectly elastic body. All particles of such body are firmly fixed in the lattice sites and are able to move in space only with the lattice as a whole (in the deformation process), not counting, of course, the oscillations of the particles around their average positions in the lattice.

A component forming a lattice with such particles is called immobile component to distinguish it from ordinary mobile components capable of migrating. Since the Maxwell velocity distribution is also fully applicable to the vibrational motion of particles in solids, we can say that the complete localization of the particles of the immobile component in the lattice is possible only at absolute zero temperature (although zero-point oscillations remain, they are typically unable to break bonds in the lattice). At a real temperature, a certain fraction of the lattice particles will inevitably pass to the mobile state. This fraction is the larger the higher is temperature.

In thermodynamics (where 'component' and 'phase' are basic notions), a solid state is defined as a phase. Then we can formulate the following definition:[2] a phase is called solid if it contains at least one immobile component. Recall that the component and the kind of particles are generally different notions. A kind of particles may be termed a component if its concentration is capable of independent variation. For example, positively charged ions of the metallic lattice may be qualified as an immobile component (and the electronic gas as a mobile component) if the electroneutrality condition is not taken into account under the terms of a problem. Otherwise the immobile component will consist of neutral particles including, like metal atoms, ions and the appropriate number of surrounding electrons. A solid material can include several immobile components. If the ratio of the immobile components is firmly fixed, their independent variation becomes impossible. Then the whole set of them can be considered as a single material-forming immobile component (we shall return to this situation below).

Unlike liquids, where pressure is uniform according to the Pascal law, the mechanical state of a solid material can be anisotropic. The mechanical state is characterized by the field of the stress tensor E_{st} and the elementary work is given by the expression

$$\sum_{s,t=1}^{3} E_{st}\mathrm{d}V_{st} = V\sum_{s,t=1}^{3} E_{st}\mathrm{d}e_{st} \qquad (2)$$

where V_{st} is the volume displacement tensor[2,3] (see also p. 266 in Ref. 4) (an analogue of the strain tensor e_{st}, V_{st} yields not a relative but the absolute change in volume). On going to a mechanically isotropic state ($E_{\mathrm{st}} = -p\delta_{st}$, $\mathrm{d}V_{st} = \mathrm{d}V$, where δ_{st} is Kronecker's delta), Eqn (2) becomes the term $-p\mathrm{d}V$ in Eqn (1).

Now we prove one of fundamental provisions of the thermodynamics of solids:[2,3] the anisotropy of stresses leads to an anisotropy of the chemical potential. Let us use a proof by contradiction. If $-p\mathrm{d}V$ is replaced by the left-hand part of expression (2) but the terms with chemical potentials remain in the initial form (as for fluids), Eqn (1) becomes

$$\mathrm{d}F = -S\mathrm{d}T + \sum_{s,t=1}^{3} E_{st}\mathrm{d}V_{st} + \sum_k X_k \mathrm{d}x_k + \sum_i \mu_i \mathrm{d}N_i \qquad (3)$$

For the sake of simplicity, we assume the material to contain the only immobile component j and external fields to be absent ($X_k = 0$). We also choose such a coordinate system (1, 2, 3) that transforms the stress tensor to the diagonal form

$$E_{st} = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}$$

where E_1, E_2 and E_3 are the principal values of the stress tensor. Equation (3) is now simplified to

$$\mathrm{d}F = -S\mathrm{d}T + E_1\mathrm{d}V_1 + E_2\mathrm{d}V_2 + E_3\mathrm{d}V_3 + \mu_j\mathrm{d}N_j \qquad (4)$$

Assuming that the material is uniform and integrating Eqn (4) successively along each principal direction at a given physical state and at fixed boundaries in other directions, we obtain

$$F = E_1 V + \mu_j N_j$$

$$F = E_2 V + \mu_j N_j$$

$$F = E_3 V + \mu_j N_j$$

This result means that the free energy density of a uniform material

$$f \equiv \frac{F}{V}$$

depends on the choice of direction of integration at $E_1 \neq E_2 \neq E_3$. However, free energy is a scalar quantity and cannot be dependent on direction. Thus, we have arrived at an absurd result after assuming that the chemical potential of a material remains isotropic in the presence of mechanical anisotropy. Obviously, each value of E_k should correspond to its own value of μ_{jk}, and the quantity

$$f = E_k + \mu_{jk}c_j$$

should be invariant with respect to the principal directions:

$$E_1 + \mu_{j1}c_j = E_2 + \mu_{j2}c_j = E_3 + \mu_{j3}c_j$$

where $c_j \equiv N_j/V$ is the concentration (the particle number density) of component j. In other words, the chemical potential of an immobile component of a solid becomes a tensor itself under the influence of the stress tensor. To be more exact, simply the tensorial nature of the chemical potential becomes visible (the chemical potential is always a tensor but is a spherical tensor for mobile components and, especially, for fluids).

In accordance with the general definition of chemical potential in chemical thermodynamics (through free energy in this case), the chemical potential tensor of an immobile component of a solid is to be defined as [2, 3] (see also p. 41 in Ref. 4)

$$\mu_{j(st)} \equiv \left(\frac{\partial F}{\partial N_{j(st)}}\right)_{T,V_{st},N_{i\neq j}} \quad (s,t = 1,2,3) \qquad (5)$$

where $N_{j(st)}$ is the mass displacement tensor that sets the algorithm of increments of the solid matter from different sides. The mass and volume displacement tensors are related to each other as [4]

$$N_{j(st)} = c_j V_{st}$$

The fact that the derivative in Eqn (5) is taken at a fixed volume displacement tensor V_{st} (rather than volume as in the thermodynamics of fluids) means the more detailed condition of fixing of all the boundaries of the system (herewith, the volume, naturally, is also fixed). The direct calculation of the chemical potential tensor *via* Eqn (5) leads to the expression [2, 3]

$$\mu_{j(st)} = v_j\left[\left(f - \sum_i \mu_i c_i\right)\delta_{st} - E_{st}\right] \qquad (6)$$

where v_j is the volume per particle of an immobile component in its lattice, and subscript i refers to mobile components (which are free to move throughout the volume of the lattice and behave like in a fluid phase) if they are present in the solid.

It follows from Eqn (6) that the chemical potential tensor becomes diagonal in the same coordinate system that diagonalizes the stress tensor. For the principal directions, Eqn (6) takes the form

$$\mu_{j(k)} = v_j\left(f - E_k - \sum_i \mu_i c_i\right) \ (k = 1,2,3) \qquad (7)$$

The sum of the principal values of the chemical potential tensor is equal to the sum of its diagonal elements (the trace of a tensor designated by Tr) in arbitrary coordinates. Then introducing the chemical potential of an immobile component

$$\mu_j \equiv \frac{1}{3}\mathrm{Tr}\mu_{j(st)} = \frac{1}{3}\sum_s \mu_{j(ss)} = \frac{1}{3}\sum_k \mu_{j(k)}$$

and, as accepted in the mechanics of continuous medium, the pressure

$$p \equiv -\frac{1}{3}\mathrm{Tr}E_{(st)} - \frac{1}{3}\sum_s E_{(ss)} = -\frac{1}{3}\sum_k E_{(k)}$$

We obtain from Eqn (7) that

$$\mu_j = v_j\left(f + p - \sum_i \mu_i c_i\right)$$

This relationship is applicable not only to a solid in a fluid medium but also to the simultaneous contact of a solid with different fluids.

It is appropriate here to remember that Gibbs, considering the contact of a soluble solid cube simultaneously with three liquids of different pressures (when only the principal stresses act in the solid), arrived at the equilibrium condition (see Ref. 5, p. 195)

$$\frac{f + p_k - \sum_i \mu_i c_i}{c_j} = \mu_j^{(k)} \ (k = 1,2,3) \qquad (8)$$

Using the mechanical equilibrium condition

$$p_k = -E_k$$

we can say that the left-hand side of Eqn (8) refers to the solid. The right-hand side is the chemical potential of the immobile component of the solid in liquid phase k (where the immobile component becomes mobile, and its chemical potential acquires a traditional scalar form). Now, by comparing Eqns (7) and (8) with taking into account the obvious relation $v_j = 1/c_j$, we can formulate the phase equilibrium condition as

$$\mu_{j(k)} = \mu_j^{(k)} \qquad (9)$$

which is the equality of the chemical potential of a solid in a dissolved state and the corresponding component of the chemical potential tensor of the solid itself.

Equation (9) shows that the left-hand side of Gibbs equation (8) can be interpreted as a principal value of the chemical potential tensor. Determining the principal values of a tensor means determining the tensor on the whole. Thus, we can say that Gibbs, who never used the term 'tensor', was the first to exhibit a tensorial nature of the chemical potential of a solid. In his formulation of Eqn (8), Gibbs avoided using the term 'chemical potential' with respect to a solid. However, he used this term later (see Ref. 5, p. 317) when considering the solubility of small solid particles (a generalization of Gibbs theory for nanoparticles was given [6]). Gibbs concluded that Eqn (8) [and, therefore, Eqn (9), too] is valid only for a flat interface and cannot be fulfilled for small solid particles with a curved surface. This paradoxical situation should be understood as follows.[7] The equilibrium condition expressed in Eqn (9) does hold true even in the case of a curved interface, but is applicable only to the surface monolayer of a solid. Because of surface tension and of the action of a curved surface, the interior of a solid particle passes to a complex state of stresses and strains. In its turn, this causes a spatial change of the chemical potential tensor of an immobile component, which cannot be levelled by diffusion since the immobile component is incapable of diffusion. As a result, the normal-to-the-surface component of the chemical potential tensor inside the particle is different from its value at the surface and in a coexisting liquid phase. Thus, we can conclude that Eqn (9) is indeed violated for a small particle when considered as the phase equilibrium condition, but remains valid for the equilibrium between a bulk liquid phase and the solid surface.

We now can interpret the chemical potential tensor at any point of a solid in the following way. Similarly to the interpretation of stress in mechanics, we have, first of all, to imagine a flat section of the solid through a given point. If the orientation of the section plane is given by unit normal vector **n**, the scalar product of **n** and the chemical potential tensor $\mu_{j(st)}$ yields the chemical potential vector $\mu_{j(\mathbf{n})}$ at this point (Fig. 1). The normal component of this vector $\mu_{j(nn)}$ is equal to the ordinary chemical potential of species j in a hypothetical equilibrium adjacent phase where species j is a mobile component. The adjacent phase can be a real liquid solution of species j for the principal directions. For other directions, the adjacent phase should be another solid containing species j as a mobile component. In this way, the chemical potential tensor of an immobile component in a solid can be directly determined from experiment.

As is seen from Eqn (8), applying the normal stress leads to decreasing the normal component of the chemical potential tensor. The action of forces in other directions is manifested through the free energy density, f, which is known to increase at any strains. If a solid is a perfectly rigid body, strains are absent, and quantity f remains constant at a fixed temperature. Then all is determined by the action of the normal stress. If, on the contrary, the normal stress is absent whereas lateral stresses lead to certain strains, the normal component of the chemical potential tensor increases. In more detail, such dependence can be derived from the fundamental equation for free energy, which, taking into account all the above, takes the following form for a solid material:

$$\mathrm{d}F = -S\mathrm{d}T + \sum_{s,t=1}^{3} E_{st}\mathrm{d}V_{st} + \sum_{s,t=1}^{3} \mu_{j(st)}\mathrm{d}N_{j(st)} + \sum_i \mu_i \mathrm{d}N_i \quad (10)$$

In the particular case of the absence of mobile components and of a fixed amount of an immobile component, Eqn (10) produces the relationship

$$\mathrm{d}\mu_{j(nn)} = -s_j \mathrm{d}T + v_j\left[\sum_{s,t=1}^{3} (E_{st} - \delta_{st}E_{nn})\mathrm{d}e_{st} - \mathrm{d}E_{nn}\right] \quad (11)$$

where $s_j \equiv S/N_j$ and $v_j \equiv V/N_j$ are entropy and volume per particle of the immobile component, respectively. We shall return to Eqn (11) below.

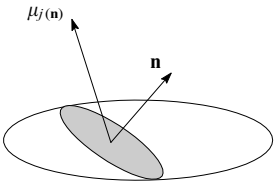


Figure 1. Chemical potential vector on an arbitrary section of a solid with unit normal **n**.

III. Chemical affinity tensor

The introduction of chemical affinity was an important step towards the practical use of chemical potential. For fluid systems, this concept was suggested by De Donder.[8, 9] Initially, chemical affinity was related to chemical reactions. The equation of a chemical reaction can be generally written as

$$\sum_i \nu'_i \mathrm{B}'_i = \sum_i \nu''_i \mathrm{B}''_i \quad (12)$$

where B_i are chemical symbols, ν_i are stoichiometric coefficients, the initial substances of the reaction being primed and the reaction products being double primed. For the sake of simplicity, the summation is carried out over all components implying that the absence of a certain substance on the left- or right-hand side of Eqn (12) is secured by the zero value of its stoichiometric coefficient. Gibbs established a very simple rule for formulating the equilibrium condition for a chemical reaction: it is enough to replace the chemical symbols by chemical potentials in the equation of a chemical reaction. Following this recipe, we can write the condition of equilibrium for Eqn (12) as

$$\sum_i \nu'_i \mu'_i = \sum_i \nu''_i \mu''_i \quad (13)$$

De Donder transferred all the terms to the left-hand side of Eqn (13) and introduced chemical affinity

$$\mathcal{A} \equiv \sum_i (\nu'_i \mu'_i - \nu''_i \mu''_i) \quad (14)$$

Now the equilibrium condition can be written as $\mathcal{A} = 0$, but the chemical affinity can also be used for characterizing non-equilibrium processes. The chemical affinity sign determines the direction of a chemical reaction. The chemical affinity value determines the rate of the reaction or, generally, of any physicochemical process. The primes have been retained in Eqn (14) since they can refer to different parts of space. For example, the chemical affinity of diffusion of species i is defined as

$$\mathcal{A}_i \equiv \mu'_i - \mu''_i \quad (15)$$

where the single and double primes refer to two fixed points in space with a given distance between them. Dividing the right-hand side of Eqn (15) by this distance yields the chemical potential gradient, which is just the driving force of diffusion.

On passing to the tensorial formalism of chemical potentials, the concept of the chemical affinity tensor appears.[2] For the above example of a chemical reaction, the definition of the chemical affinity tensor is

$$\mathcal{A}_{st} \equiv \sum_i (\nu'_i \mu'_{i(st)} - \nu''_i \mu''_{i(st)})$$

The chemical potential tensors are symmetrical and the chemical affinity tensor is a linear combination of the chemical potential tensors, hence, it should also be symmetrical and, therefore, it can be reduced to the diagonal form. If the solid lattice contains several immobile components, their chemical potential tensors are 'tuned' by the same stress tensor in each local area of the lattice. For this reason, they are easily added and simultaneously diagonalizable. If the proportion of immobile components in a material is strictly determined by stoichiometric coefficients $\nu_1, \nu_2, \nu_3, \ldots$, the whole set of the immobile components can be treated as a single material-forming component with the chemical potential tensor given by

$$\mu_{j(st)} \equiv \nu_1 \mu_{1(st)} + \nu_2 \mu_{2(st)} + \nu_3 \mu_{3(st)} + \ldots.$$

In this case, the assumption of the uniqueness of the immobile component never reduces the generality of the theory.

Since the particles of an immobile component cannot leave their sites in the lattice, the mechanism of levelling of chemical potentials by means of migration does not act in a perfectly elastic solid. For this reason, although the chemical potential tensor can change from point to point inside a material even in the equilibrium state, the corresponding chemical affinity tensor is of no practical significance. A different situation arises at the material surface where the immobile component is capable of acquiring mobility. Such process is governed by the affinity [4]

$$\mathcal{A}_j = \mu^{\alpha}_{j(nn)} - \mu^{\beta}_j \tag{16}$$

where $\mu^{\alpha}_{j(nn)}$ is the normal (to the surface) component of the chemical potential tensor of immobile species j at the boundary between solid body α and adjacent phase β where species j is a mobile component. The simplest example of such process can be dissolution of a material in a liquid at $\mathcal{A}_j > 0$ or deposition of a substance from solution at $\mathcal{A}_j < 0$ when, on the contrary, the mobile particles become immobilized. In this case, the surface normal **n** becomes a principal direction for the chemical potential tensor when Eqn (7) acts at $\mu^{\alpha}_{j(nn)} \equiv \mu^{\alpha}_{j(n)}$ $(k = n)$. If the process driven by the affinity shown in Eqn (16) ends with a state of equilibrium, we arrive at the condition [4]

$$\mathcal{A}_j = 0, \ \mu^{\alpha}_{j(nn)} = \mu^{\beta}_j \tag{17}$$

Equation (17) is equivalent to Gibbs equilibrium condition, Eqn (13), for the case of the process of dissolution/deposition in a liquid.

Since stresses and strains have a direct impact on the chemical potential tensor and quantity $\mu^{\alpha}_{j(n)}$, they also influence the rate of dissolution. Any strains increase the free energy density f in Eqn (6) and, as a consequence, chemical potential $\mu_{j(n)}$. As for the direct action of stress $E_{(k)} = E_{(n)}$ it can be only the pressure on the side of a liquid, which is opposite in sign to stress $(E_{(n)} = -p)$ and, therefore, also works to increase the chemical potential. The latter causes an increase in the chemical affinity, which, in its turn, increases the dissolution rate. Thus, we come to the conclusion that every strain of a material accelerates its dissolution.

Besides dissolution, various chemical reactions can occur at the contact of a material with a chemically active medium. Each reaction is governed by its own chemical affinity of type of Eqn (14). Both immobile and mobile components can simultaneously participate in such reactions. Influencing the chemical potentials and affinity, stresses and strains also affect the rate of chemical reactions. Studying such effects is the goal of mechanochemistry, which is very close to and important for materials science. Below we shall consider the corrosion of materials as an example of the most important reactions, but now we are interested in the interaction of mobile and immobile components.

In this Section, we have traced this interaction at the material boundary. However, the interaction and mutual transformation of mobile and immobile components can also occur in the interior of a material. It is linked to the appearance of such an important material property as creep. Below, not touching upon the modern theories of creep, we shall see what interpretation of this interesting phenomenon can be expected from chemical thermodynamics.

IV. Creep of materials

So as not to obscure the essence of the matter and not be distracted by such details as lattice defects, grains, *etc.* (although they can be important for practice), we confine our consideration to a solid of an ideal crystalline lattice. For the manifestation of creep, not merely the presence of mobile components is important but the presence of mobile components of the same nature as those in the solid lattice. To distinguish such mobile components from extraneous mobile components, we shall call them *intrinsic* mobile components. As we already mentioned in the Introduction, the existence of thermal vibrations of particles in the lattice sites leads to the situation when a certain fraction of the particles inevitably goes into mobile state. These are, evidently, the particles whose kinetic energy exceeds the bond energy in the lattice. We can calculate the fraction of such particles with the aid of the Maxwell distribution of statistical mechanics

$$\rho(\mathbf{p}) = (2\pi mkT)^{-3/2} \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right)$$

where **p** is the vector of the particle momentum, $\rho(\mathbf{p})$ is the probability density in the momentum distribution, m is the particle mass and k is the Boltzmann constant. At a given temperature T, the Maxwell distribution always includes particles with kinetic energy $p_k^2/2m$ (p_k are the momentum components, $k = x, y, z$) larger than the bond energy ε in the lattice. Accounting for the independence of distributions of the momentum components, the fraction x_m of such particles can be represented by the expression

$$x_m = \frac{1}{\pi^{3/2}} \left[2 \int_{(2m\varepsilon)^{1/2}}^{\infty} \frac{\mathrm{d}p_k}{(2mkT)^{1/2}} \exp\left(-\frac{p_k^2}{2mkT}\right)\right]^3 = \tag{18}$$

$$= \left[\frac{2}{\pi^{1/2}} \int_{(\varepsilon/kT)^{1/2}}^{\infty} \exp\left(-t^2\right) \mathrm{d}t\right]^3 = \mathrm{erfc}^3\left[\left(\frac{\varepsilon}{kT}\right)^{1/2}\right]$$

where p_k is any of the momentum components, $t \equiv p_k/(2mkT)^{1/2}$, factor 2 appears because we integrate only over positive momentum values (there is the similar integral on the side of negative values). Quantity erfc is the complementary error function, which is related to the ordinary error function erf as

$$\mathrm{erfc} = 1 - \mathrm{erf} \tag{19}$$

$$\mathrm{erf}(x) \equiv \frac{2}{\pi^{1/2}} \int_0^x \exp\left(-t^2\right) \mathrm{d}t$$

$$\frac{2}{\pi^{1/2}} \int_0^\infty \exp\left(-t^2\right) \mathrm{d}t = 1$$

The plot of x_m *vs.* $(\varepsilon/kT)^{1/2}$ is shown in Fig. 2. In the limit of high temperatures when the abscissa becomes zero, $x_m = 1$, *i.e.*, all particles of the lattice are mobile. This means that we have no solid, there is a fluid. As the temperature decreases, the major changes take place within the interval $0 \leqslant \varepsilon/kT \leqslant 1$. We already have $x_m = 0.00389$ at $\varepsilon/kT = 1$. With further lowering the temperature, the fraction of the intrinsic mobile component only changes from a negligible value to still more negligible value. This means that the model of a perfectly elastic solid can serve as a good approximation in a rather wide range of temperatures far from the melting point. Nevertheless, in any whatsoever amount, intrinsic mobile components are present. Equations (18) and (19) strictly yield $x_m = 0$ only at the absolute zero temperature.

Since creep is related to diffusion, which can involve only mobile components, the above estimation shows that the proximity to the melting point is very important for the manifestation of creep. We now consider a solid material at a sufficiently high temperature. For the sake of simplicity, we assume the material to contain only one immobile component and one intrinsic mobile component. In the absence of stress, both the components are uniformly distributed over the volume and are in a mutual equilibrium according to the above calculation. The equilibrium implies equality of their chemical potentials in all directions. As a consequence, the chemical potential tensor of the immobile component is isotropic to obey the relationship

$$\mu_{j(st)} = \mu_j \delta_{st}$$

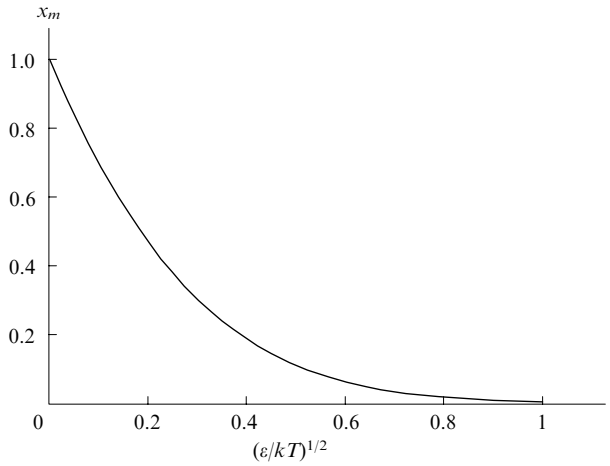


Figure 2. Fraction of the intrinsic mobile component x_m as a function of $(\varepsilon/kT)^{1/2}$ according to Eqn (18).

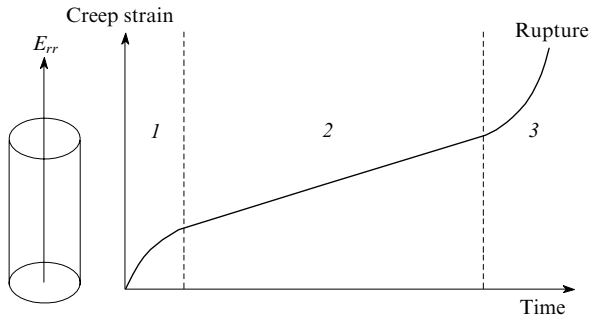


Figure 3. Typical experimental dependence of the creep strain on time: (*1*) primary creep, (*2*) steady creep, (*3*) necking and rupture.

where μ_j is the chemical potential of the intrinsic mobile component.

We now imagine that an external force is applied to the body under consideration. In a classic stretching cylinder experiment (we assume the cylinder to be oriented in a direction r, Fig. 3), a stress E_{rr} appears, which has a dual effect. First, a pure mechanical strain occurs. This is a very fast process for an elastic body with the final establishment of mechanical equilibrium. Second, the stress E_{rr} leads to a decrease in the component of the chemical potential tensor of the immobile component in the direction r down to a value $\mu_{j(rr)}$. In its turn, this gives rise to the component of the chemical affinity tensor

$$\mathcal{A}_j = \mu_j - \mu_{j(rr)}$$

which stimulates the transition of matter into the lattice along the direction r. This affinity is valid everywhere. However, the lattice is completely filled in the bulk, and matter is simply unable to enter it. The only places where the intrinsic mobile component can be incorporated into the lattice are the ends of the cylinder. Naturally, the intrinsic mobile component migrates there. The part of the intrinsic mobile component initially located near the ends is consumed first, and the cylinder slightly elongates. This is the rapid stage of creep (the primary creep, Fig. 3). The result of the first stage is an abrupt drop of concentration of the intrinsic mobile component near the cylinder ends and the appearance of the concentration gradient in the bulk and on the lateral cylinder surface. Then the conventional diffusion affinity, Eqn (15) with $i = j$, comes into effect, and the increment of the lattice at the cylinder ends develops upon receipt of new portions of the intrinsic mobile component by diffusion. This long stationary process forms a slow creep stage (the steady creep, Fig. 3). In the course of the second stage, particles from the lateral surface of the cylinder, after their transition to mobile state under the influence of thermal motion, join the diffusion flux. As a result, the cylinder diameter decreases, and the cylinder length increases. If the stress is not removed, the case ends with the rupture of the cylinder. Thus, we can conclude that thermodynamics explains the essence of the creep phenomenon and its characteristic features.

V. Corrosion of materials. Role of surface

Every corrosion is a certain chemical reaction or a set of reactions. In most cases, a solid material reacts with the surface, which makes important the knowledge of the chemical potential of matter at the surface. Addressing the interaction between a solid and a fluid medium, we can

again use the normal component, $\mu_{j(nn)}$, of the chemical potential tensor. This quantity appears in the chemical affinity of a chemical reaction, Eqn (14), which, in this case, can be represented as

$$\mathcal{A} \equiv \mu_{j(nn)} + \sum_i (\nu_i{}' \mu_i' - \nu_i{}'' \mu_i'')$$

where the subscript i refers to all other participants of the reaction. Their state is determined by the fluid medium and is independent of the state of the solid. Therefore, if the material is subjected to deformation, this can affect only the magnitude of $\mu_{j(nn)}$. Then we have [2]

$$\mathrm{d}\mathcal{A} = \mathrm{d}\mu_{j(nn)} \tag{20}$$

Equation (20) leads to the important conclusion: to learn how the deformation of a material influences the rate of a chemical reaction, it is sufficient to study the behaviour of the normal component, $\mu_{j(nn)}$, of the chemical potential tensor of the material. If $\mu_{j(nn)}$ increases, the reaction rate increases too. If $\mu_{j(nn)}$ decreases, the reaction is retarded.

Let us illustrate this with the example of iron corrosion. The reaction of the anodic dissolution of iron is as follows:

$$\mathrm{Fe} = \mathrm{Fe}^{2+} + 2\,\mathrm{e}$$

The corresponding chemical affinity is given by the expression

$$\mathcal{A} = \mu_{\mathrm{Fe}(nn)} - \mu_{\mathrm{Fe}^{2+}} - 2\,\mu_{\mathrm{e}} \tag{21}$$

where $\mu_{\mathrm{Fe}(nn)}$ is the normal component of the chemical potential tensor of iron in a solid state on the surface, $\mu_{\mathrm{Fe}^{2+}}$ is the chemical potential of the iron ion in solution, and μ_{e} is the chemical potential of electron. The quantity $\mu_{\mathrm{Fe}^{2+}}$ is determined by the solution composition and is independent of the mechanical state of a solid sample. As for the electron chemical potential, it, although refers to a solid, can be controlled independently of the lattice state (*e.g.*, by specifying an electric potential) since electrons form a mobile component of a metal. Thus, only the chemical potential μ_{Fe} on the right-hand side of Eqn (21) has a direct influence of the deformation of the sample. The higher the chemical potential of iron in the solid state, the larger the chemical affinity and, therefore, the higher is the rate of corrosion.

Now, using Eqn (20), we shall see how the strain of a material influences the rate of a chemical reaction. Let us return to Eqn (11). To apply it, we assume that mobile components (including intrinsic ones) are absent. This means that we consider a material in a state far from the melting point, and the model of a perfectly elastic body does work. The amount of a material can change in the course of a chemical reaction. However, for using Eqn (11), we have to set the material amount constant in that sense that we compare the reaction rates for a given amount of a material in non-deformed and deformed states. Because the material surface is facing the external fluid medium, the term $-E_{nn}$ in Eqn (11) is nothing else than the external pressure, which can be considered constant. Finally, we assume that the reaction proceeds slowly enough to stay under isothermal conditions (corrosion refers specifically to such reactions). Taking into account all the above, in our case, Eqn (11) takes the form [2]

$$\mathrm{d}\mu_{j(nm)} = \nu_j \sum_{s,t=1}^{3} (E_{st} - \delta_{st} E_{nn}) \mathrm{d}e_{st} > 0 \tag{22}$$

The right-hand side of Eqn (22) is positive, as it is the work of material strain (per particle in the lattice) performed by additional (to the external pressure) forces. Accounting for Eqn (20), we then arrive at the conclusion that any deformation of a solid material accelerates the corrosion (and, in general, accelerates any other chemical reaction in which the material plays the role of an initial substance). It is of note that acceleration of metal corrosion was observed experimentally for a number of simple types of strain a long time ago (see, *e.g.*, Ref. 10 and references therein). As for thermodynamics, it makes a similar prediction for a broad category of materials and reactions.

In the above problem, there are more subtle effects associated with the surface. More precisely, it concerns surface tension, which is defined as an excess surface stress. Continuum mechanics usually ignores the existence of surface tension. However, every body of finite dimensions possesses surface tension, which forms due to internal forces. To avoid erroneous conclusions, surface tension should be taken into account in materials science. For illustration, we consider this issue as an example of corrosion of a bent steel plate. In such a plate, the convex side is stretched and the concave side is compressed. Let us turn first to the convex side. Choosing the principal directions 1 and 2 as coordinate axes, we write Eqn (22) for this case as [2]

$$\mathrm{d}\mu_{j(nn)} = \nu_j (E_{11}\mathrm{d}e_{11} + E_{22}\mathrm{d}e_{22}) = \nu_j (E_{11} - \kappa_{21} E_{22}) \mathrm{d}e_{11} \tag{23}$$

where the subscript 1 refers to the stretching direction (Fig. 4) and the subscript 2 refers to the transverse direction; in accordance with Eqn (22), the stresses E_{kk} ($k = 1, 2$) are now measured from the normal stress E_{nn}, *i.e.*, actually they are tensions; $\kappa_{21} \equiv -\mathrm{d}e_{22}/\mathrm{d}e_{11}$ is the corresponding Poisson ratio.

Equation (23) is related to particles in the surface monolayer, where surface tension γ acts. To be more exact, surface tension acts in the entire interfacial region, capturing also the underlying monolayers. But the lion's share of the surface tension just falls on the surface monolayer. It will be this share that will be designated as γ in this paper. In other words, γ is the real tension (excess stress) in the surface monolayer of a material in the absence of strain. Then we may split each of the quantities E_{11} and E_{22} in Eqn (23) into two terms:[2]

$$E_{11} = \gamma + \lambda_{1111} e_{11} \tag{24}$$

$$E_{22} = \gamma + \lambda_{2211} e_{11} \tag{25}$$

The first term in Eqns (24) and (25) is the initial tension (assumed to be isotropic for the sake of simplicity) that was in the surface monolayer of the plate before bending. The second term is a tension acquired during the deformation. For an elastic material, this tension is proportional to the strain e_{11} (λ_{1111} and λ_{2211} are the corresponding components of the elasticity modulus tensor). As a result, Eqn (23) for the convex side of the plate becomes

$$\mathrm{d}\mu_{j(nn)} = \nu_j \left[\gamma(1 - \kappa_{21}) + \lambda e_{11}\right] \mathrm{d}e_{11} \tag{26}$$

where a specific elasticity modulus is defined as $\lambda \equiv \lambda_{1111} - \kappa_{21}\lambda_{2211}$.

We now turn to the concave side of the plate where the contraction occurs. It is known from the theory of elasticity that small deformations of stretching and contraction on the opposite sides of a bent thin plate are perfectly symmetrical. Therefore, we can also use Eqn (26) for the concave side (we shall mark the concave side with a prime)

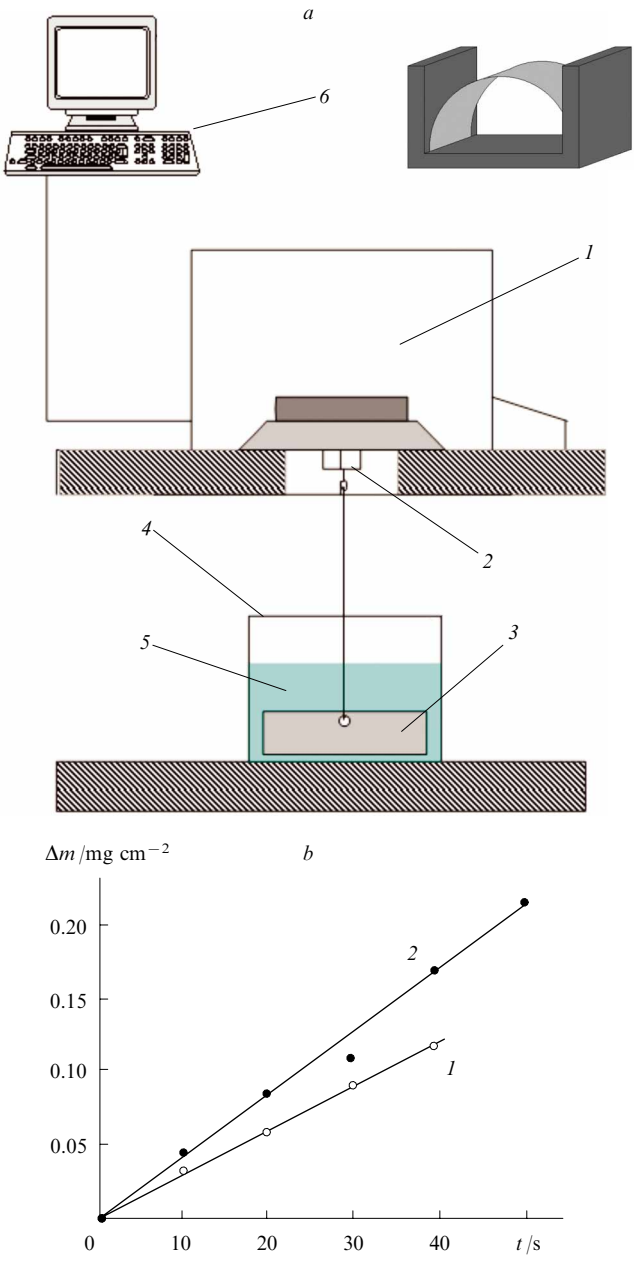


Figure 4. Measuring the rate of corrosion of a bent steel plate by weight (*a*) and resulting plot for the convex and concave sides of the plate (*b*);[11–13]
(*a*) (*1*) electronic balance, (*2*) special device for suspending a load, (*3*) frame with a bent plate, (*4*) vessel, (*5*) corroding liquid medium, (*6*) computer for simultaneous recording and processing of the results (6);
(*b*) Δm is mass loss per unit area, t is time; plate sides: (*1*) convex, (*2*) concave.

by setting $e'_{11} = -e_{11}$. Then we obtain for the concave side of the plate

$$\mathrm{d}\mu'_{j(nn)} = \nu_j\left[\lambda e_{11} - \gamma(1-\kappa_{21})\right]\mathrm{d}e_{11} \tag{27}$$

where the quantity e_{11} still refers to the convex side. From the comparison of Eqns (26) and (27), it is seen that $\mathrm{d}\mu_{j(nn)} \neq \mathrm{d}\mu'_{j(nn)}$. Since the expressions for these quantities differ only in the strain sign, one can say that, in the corrosion phenomenon (and in the mechanochemistry of materials as a whole), there exists not only the effect of strain, but also the effect of the strain sign. From Eqns (26) and (27), we have [2]

$$\frac{\mathrm{d}\mu_{j(nn)}}{\mathrm{d}\mu'_{j(nn)}} = \frac{\lambda e_{11} + \gamma(1-\kappa_{21})}{\lambda e_{11} - \gamma(1-\kappa_{21})} \tag{28}$$

Equation (28) gives evidence that it is just surface tension that is the cause of the mechanochemical effect of the strain sign: Eqn (28) at $\gamma = 0$ yields

$$\frac{\mathrm{d}\mu_{j(nn)}}{\mathrm{d}\mu'_{j(nn)}} = 1$$

The surface tension is always positive for liquids, but can be of any sign for solids. This should be taken into account for analyzing Eqn (28). Thus we can formulate the following thermodynamic rule:[2,3] the corrosion rate should be higher on the convex side than on the concave side if surface tension is positive, and, the reverse, the corrosion rate should be higher on the concave side if surface tension is negative.

This thermodynamic prediction was confirmed experimentally. The mechanochemical effect of the strain sign in the phenomenon of corrosion under stress was discovered quite recently.[11–14] The experiments were carried out with

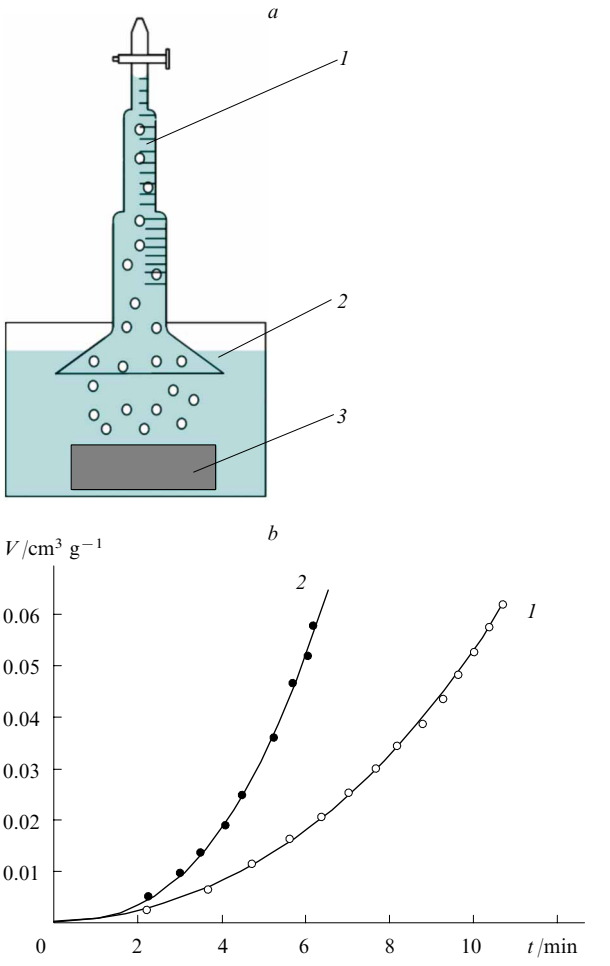


Figure 5. Measuring the rate of corrosion of a bent steel plate by the hydrogen volumetry (*a*) and resulting plot for the convex and concave sides of the plate (*b*);[11–13]
(*a*) (*1*) three-stage burette with hydrogen bubbles, (*2*) acidic corroding medium, (*3*) frame with a bent steel plate; *b*: V is volume of the gas, t is time; plate sides: (*1*) convex, (*2*) concave.

bent steel plates in aqueous solutions of hydrochloric and sulfuric acids. The rate of corrosion was measured either directly *via* the plate weight (Fig. 4) or with the aid of the hydrogen volumetric technique (Fig. 5). Both the methods showed that corrosion proceeded faster on the concave side at the initial stage. However, the reversal of the situation occurs in the course of time, and the corrosion becomes faster on the convex side of the plate . This fact is trivial and obviously related to the phenomenon of cracking of the convex side of the plate, the typical companion of corrosion. As a result of cracking, the surface roughness and the effective contact area with the solution increase for the plate convex side. Correspondingly, the density of the flux of iron ions from the visible surface to solution increases too, which makes the convex side prevailing. It is of note that implementation of the phenomenon of the reversal of behaviour of the convex and concave sides of a bent steel plate depends on what kind of an alloy steel is used. Stainless steel (*e.g.*, austenite steel) where the process of corrosion develops very slowly, can exhibit the prevalence of the concave side of a bent plate for a long time as is shown in Fig. 5.

At the initial stage of corrosion, we deal with a smooth surface. As it follows from the comparison of the corrosion rate on the convex and concave sides of the plate, the initial surface tension at the contact of the flat plate (before bending) with solution is negative. This is easily explained by the formation of the electrical double layer that is composed of the negatively charged metal surface and positive iron ions adsorbed from solution. Likely charged ions of the electric double layer, both in the solid lattice and in the adsorbed layer, repel each other, and this creates a negative surface tension.

VI. Strength of materials

Strength is one of the most important properties of materials. Beginning from the first work by Griffith [15] and up to the present time, the theory of strength has been based on three pillars: mechanics, thermodynamics and surface science. Mechanics is needed for calculating the elastic energy of a loaded material with a crack, especially the distribution of elastic energy near the crack, because the crack growth and the fracture of a material partly proceed at the expense of elastic energy. Griffith considered the contribution of elastic energy of Hookean nature as a positive quantity. However, it is not the strain work itself but an excess of elastic energy with respect to a crack that is needed for calculations, and such a quantity is negative. This mistake was corrected by Sack,[16] who considered a circular ('penny-shaped') crack. Summing up the results of Sack and Griffith (for a rectilinear crack), we can write the excess elastic energy per unit crack length for a body loaded with stress P normally to the crack plane as

$$w = -bP^2c^2 \tag{29}$$

where c is the crack depth (the crack radius in the case of a circular crack) and b is an elastic constant:
for a circular crack,

$$b = \frac{4(1-\nu^2)}{3\pi Y}$$

and for a rectilinear crack,

$$b = \frac{\pi\nu}{2Y}$$

(Y is the Young modulus and ν is the Poisson ratio).

After comparison of these two important cases, one can say that Eqn (29) with an appropriate constant b seems to be applicable to a crack of an arbitrary shape.

Surface science is also needed since cracking is the formation of a new surface. We considered surface tension γ as an excess stress per unit surface area in the preceding section; γ can also be interpreted as the work of stretching the surface area by unity. The work of creating a unit new surface (σ) by cracking is also often called surface tension.[15] For liquids, $\sigma = \gamma$ but these quantities are different for solids. Thermodynamically, σ is strictly defined as the excess grand thermodynamic potential per unit surface.[17] Since γ is a pure mechanical quantity while σ follows a thermodynamic definition, they can be termed as the mechanical or thermodynamic surface tension, respectively.[18, 19] Every crack has not only surfaces, but also the front line, which is characterized energetically by line tension. This quantity is also defined in two manners: as the work of stretching an already existing old line by unit length (mechanical line tension, τ) or as the work of creating a new unit-length line (thermodynamic line tension, κ). Evidently, both the thermodynamic surface tension σ and the thermodynamic line tension κ are needed for formulating a full theory of cracking.[20–23]

Thermodynamics plays a central role in constructing a theory of material strength. The goal of thermodynamics is calculating the work of cracking as a function of the crack depth for a solid under load. This work passes through a maximum point, which corresponds to the ultimate strength. This means that a crack even only slightly exceeding the crack depth at the maximum point will grow spontaneously. In turn, this leads to the fracture of the material. The situation very much resembles the thermodynamics of phase transitions where the work of formation of a new-phase embryo passes through a maximum, after which the embryo spontaneously grows to a macroscopic phase.

How is work calculated in thermodynamics? Griffith seemed not to be acquainted with thermodynamics or, at least, with Gibbsean thermodynamics. He dealt with general physical quantities, such as energy or potential energy. Meanwhile, Gibbsean thermodynamics claims that every work can be found as an increment of a certain thermodynamic potential. Which of thermodynamic potentials should be used depends on external conditions. In the 20th century, five thermodynamic potentials were most popular: energy U, free energy F, enthalpy H, Gibbs energy (free enthalpy) G and grand thermodynamic potential Ω. Equations (30)–(34) show how these functions are defined and under the constancy of what external parameters (shown in parentheses) they become thermodynamic potentials (otherwise they remain to be ordinary thermodynamic characteristic functions):

$$U \quad (S, V_{st}, N_{j(st)}, N_i) \tag{30}$$

$$F \equiv U - TS \quad (T, V_{st}, N_{j(st)}, N_i) \tag{31}$$

$$H \equiv U + pV \quad (S, p, N_{j(st)}, N_i) \tag{32}$$

$$G \equiv U - TS + pV = F + pV = H - TS \quad (T, p, N_{j(st)}, N_i) \tag{33}$$

$$\widetilde{\Omega} \equiv U - TS - \sum_i \mu_i N_i = F - \sum_i \mu_i N_i \quad (T, V_{st}, N_{j(st)}, \mu_i) \tag{34}$$

All these quantities originate from the thermodynamics of fluids. In particular, the definition in Eqn (34) includes only mobile components. As applied to solids, this means

that we deal, in reality, with a hybrid function (designated as $\widetilde{\Omega}$) that is grand thermodynamic potential only with respect to mobile components, but is free energy with respect to the immobile component of a solid.[24] However, a rigorous definition of the true grand thermodynamic potential Ω of a solid is also possible by adding the term $-\mu_{j(n)}N_j$ to Eqn (34).[17] Similarly, the origin from the thermodynamics of fluids is shown by using only pressure (not the stress tensor) in Eqns (32) and (33). As applied to solid materials, p can be understood as an external pressure in these definitions.

A typical strength test consists of loading a solid. However, none of Eqns (30)–(34) is suitable for this case. Indeed, the constancy of the volume displacement tensor, V_{st} in Eqns (30), (31) and (34) prohibits any deformation but strain accompanies loading of a real solid by necessity. Therefore, strictly speaking, energy, free energy and grand thermodynamic potential cannot serve as thermodynamic potentials in any strength theory. The two remaining thermodynamic potentials, enthalpy and Gibbs energy, correspond only to the simplest case of loading, namely, a uniform external pressure, and cannot serve as thermodynamic potentials, say, in the case of uniaxial loading. Thus, we can conclude that the classical thermodynamic potentials are insufficient for constructing a theory of strength. For this reason, some novel thermodynamic potentials were suggested.

The first step was introducing directed partial quantities.[2,3] Here the term 'directed' does not mean that a quantity becomes a vector. All directed thermodynamic potentials remain scalars, but their definitions are related to a certain direction in space. For example, directed Gibbs energy G_r is defined as

$$G_r \equiv F - E_{rr}V \tag{35}$$

where r is the direction of loading and E_{rr} is the loading stress. This is a simple case since E_{rr} is a tensile stress, and Eqn (35) is an analogue of the conventional definition of Gibbs energy given in Eqn (33). More complex definitions were discussed in the literature[21] but remain far from practical use. The definition expressed in Eqn (35) corresponds to uniaxial loading. We confine our consideration to this case.

Taking then G_r as a thermodynamic potential and accounting for the elastic energy, Eqn (29), and the thermodynamic surface and line tensions, σ and κ, we write an expression for the work of the crack growth as[20–23]

$$\frac{\mathrm{d}G_r}{\mathrm{d}c} = \sigma\frac{\mathrm{d}A_c}{\mathrm{d}c} + L\frac{\mathrm{d}(\kappa+w)}{\mathrm{d}c} + (\kappa+w)\frac{\mathrm{d}L}{\mathrm{d}c} \tag{36}$$

where c is the crack depth, A_c is the crack surface area, and L is the length of the crack front line. Using the geometrical relationships

$$\mathrm{d}A_c = 2L\cos\phi\,\mathrm{d}c$$

and

$$\frac{\mathrm{d}\ln L}{\mathrm{d}c} = \frac{1}{R}$$

(2ϕ is the tip angle of the crack, R is the local curvature radius of the crack front line), Eqn (36) is rearranged to the form

$$\frac{\mathrm{d}G_r}{\mathrm{d}c} = L\left(2\sigma\cos\phi + \frac{\mathrm{d}w}{\mathrm{d}c} + \frac{\kappa+w}{R} + \frac{\mathrm{d}\kappa}{\mathrm{d}c}\right) \tag{37}$$

The criterion of brittle fracture requires that

$$\frac{\mathrm{d}G_r}{\mathrm{d}c} < 0$$

Using Eqns (37) and (29) with $\mathrm{d}w/\mathrm{d}c = -2bP^2c$ we can write the criterion of brittle fracture as

$$2\sigma\cos\phi - 2bP^2c + \frac{\kappa+w}{R} + \frac{\mathrm{d}\kappa}{\mathrm{d}c} < 0 \tag{38}$$

The value of the derivative $\mathrm{d}\kappa/\mathrm{d}c$ in Eqns (37) and (38) depends on the mechanism of the crack growth. Two particular mechanisms were qualified in the literature[21–23,25] as conformal and depth growth of a crack. The conformal mechanism corresponds to the constancy of the crack tip angle when the crack remains geometrically similar to itself at all stages of its propagation (Fig. 6 *a*). In this case, the thermodynamic line tension is sensitive to the crack depth only at nanoscale, unless the distance between the crack lips exceeds the length of action of molecular forces. Beyond this range, the condition

$$\frac{\mathrm{d}\kappa}{\mathrm{d}c} = 0$$

is fulfilled both for microscopic and macroscopic cracks. The mechanism of the depth growth implies the constancy of the distance between the crack lips. In this case, the tip angle of a crack monotonically decreases with increasing the crack depth (Fig. 6 *b*). As a consequence, the molecular force fields of the crack walls overlap to an increasing degree, and the thermodynamic line tension changes (being typically negative, increases in its absolute value) so that

$$\frac{\mathrm{d}\kappa}{\mathrm{d}c} \neq 0$$

Griffith neglected the line tension, but we see that κ also disappears from Eqn (37) when the crack front line is rectilinear ($R = \infty$) and the crack propagates conformably (then $\mathrm{d}\kappa/\mathrm{d}c = 0$ as it was noticed first by Hatzitrifon and Gdoutos.[26] In this case, Eqn (38) is simplified to

$$\sigma\cos\phi - bP^2c < 0 \tag{39}$$

For $\cos\phi = 1$ (Griffith considered an infinitely narrow crack with $\phi = 0$) Eqn (39) corresponds to Griffith's criterion. Thus, we see that, despite neglecting the line tension, Griffith's result for the ultimate strength

$$E_t = \left(\frac{\sigma}{bc}\right)^{1/2}$$

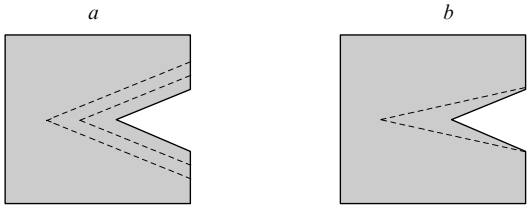


Figure 6. Conformal (*a*) and depth (*b*) mechanisms of the crack growth.

remains valid for the conformal growth of a crack beyond the nanoscale.[26] However, the thermodynamic analysis[21,22,25] shows the conformal growth to be energetically unfavourable. It can be seen from Fig. 6 on comparing cracks with the same initial width (the distance between the crack lips) and with the same final depth that the crack of the depth mechanism always lies inside the crack of the conformal mechanism. Therefore, the former requires smaller work for its propagation than the latter. So it is most probable that a crack grows more in depth than in width. Then accounting for the derivative in Eqns (37) and (38) becomes mandatory in a rigorous theory and leads to the criterion

$$E_t = \left(\frac{2\sigma\cos\phi + \mathrm{d}\kappa/\mathrm{d}c}{2bc}\right)^{1/2}$$

As for the practical aspect, the correction related to the line tension is, naturally, small for macroscopic cracks, but can be of significance for nanocracks[21–23] the presence of which is important for the problem of strength of materials.

The above thermodynamic potentials are well suitable in the case when cracking occurs in a vacuum or in the air. If the air contains some vapours, capillary condensation can occur in a crack. A symmetrical phenomenon, capillary evaporation,[27–31] develops when cracking of a solid happens in a non-wetting or slightly wetting liquid. In both the cases, a phase transition occurs in a crack.[32] As a result, two phases, α and β, coexist inside a crack with an interface $\alpha\beta$ between them and the contact angle θ characterizing the wettability of the crack walls (Fig. 7).

The theory of capillarity requires that, in any case, the $\alpha\beta$ interface should be convex with respect to the crack tip and the following angular relationships should be fulfilled:[32]

$$\theta < \frac{\pi}{2} - \phi \text{ (capillary condensation)}$$

$$\theta > \frac{\pi}{2} + \phi \text{ (capillary evaporation)}$$

Although the two cases are symmetrical, the lack of coincidence of these inequalities is explained by the procedure that the contact angle is always measured on the side of a liquid. If the condition

$$\frac{H}{2} > \frac{r}{\left[1 + \mathrm{tg}(\pi - \theta + \phi)\right]^{1/2}}$$

(r is the curvature radius of the $\alpha\beta$ interface and H is the maximum crack width, Fig. 7) is satisfied, a liquid meniscus as a whole penetrates the crack interior. For us, this is the third case when the fracture of a material takes place in a wetting liquid that completely fills a crack.

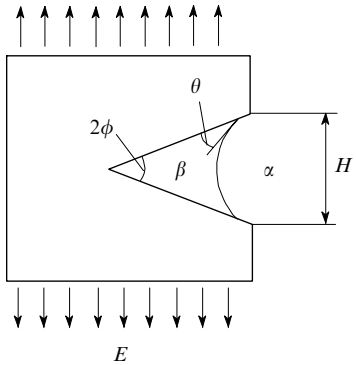


Figure 7. Loaded material with a wedge-shaped rectilinear crack containing phase α as a surrounding medium and phase β as a result of capillary condensation (if α is a gaseous phase) or capillary evaporation (if α is a liquid phase).
θ is the contact angle for the case of capillary condensation (it would be $\pi-\theta$ in the case of capillary evaporation), 2ϕ is the tip angle of the crack, H is the distance between the crack lips and E is the loading stress.

All the three cases are characterized by the condition that the components of a liquid medium can retain their chemical potentials inside the crack. This means that one more novel potential, similar to grand thermodynamic potential, is needed for describing the process of cracking in a liquid medium. Such a potential has been recently introduced and named J-potential.[33] In our case of uniaxial loading, the corresponding J-potential (J_r) is defined as

$$J_r \equiv \Omega - E_{rr}V = F - E_{rr}V - \sum_i \mu_i N_i - \mu^{\alpha}_{j(rr)} N_j \qquad (40)$$

where the superscript α refers to the solid phase. This definition uses the normal component of the chemical potential tensor of the immobile component of a solid as a variable. This can be inconvenient in some cases. For this reason, proceeding from the hybrid grand thermodynamic potential $\widetilde{\Omega}$, the hybrid J-potential ($\widetilde{J}$) was also introduced,[34] which looks in our case as

$$\widetilde{J}_r \equiv \widetilde{\Omega} - E_{rr}V = F - E_{rr}V - \sum_i \mu_i N_i \qquad (41)$$

(only the chemical potentials of mobile components are retained). The potential $\widetilde{J}_r$ acts as grand thermodynamic potential with respect to mobile components and as free energy with respect an immobile component of a material. For a one-phase fluid homogeneous system, considering that $\Omega = -pV$, Eqns (40) and (41) yield

$$J_r = \widetilde{J}_r = \Omega + pV = 0$$

In other words, the J-potential does not exist for such simple systems. But it simplifies the description of more complex systems, such as solid or heterogeneous (composite) materials.

Let us see how the theory of the ultimate strength of materials is formulated in this case. For the sake of simplicity, we consider the case of a uniaxial stress under atmospheric pressure. This means inclusion of two forces: the uniform external pressure p and a loading stress $E \equiv E_{rr}$ in direction r perpendicular to the mean crack plane (Fig. 7). Then, combining the definitions expressed in Eqns (33) and (35), we have for $\widetilde{J}_r$ in this case

$$\widetilde{J}_r \equiv \widetilde{\Omega} + p^{\alpha}V - EV \qquad (42)$$

where the phase superscript α refers to the surrounding medium and, naturally, the stress E is measured from the outer pressure. The potential $\widetilde{J}_r$ would be again zero if the material contained only a homogeneous solid phase. However, we have, in addition, a crack in the solid and two fluid phases, α and β, inside the crack. Introducing superscript s for the solid part of the system and phase volumes

$$V^{\mathrm{s}} + V^{\alpha} + V^{\beta} = V$$

we can write Eqn (42) explicitly as

$$J_r = J_r^s + (p^\alpha - p^\beta)V^\beta + \sigma^\alpha A^\alpha + \sigma^\beta A^\beta + \gamma A^{\alpha\beta} + \kappa L \qquad (43)$$

where σ^α and σ^β are the macroscopic values of thermodynamic surface tensions of the crack walls in contact with phases α and β, A^α and A^β are the total contact areas, γ ($= \sigma^{\alpha\beta}$) is surface tension at the boundary $\alpha\beta$ (the surface tension of the meniscus), and $A^{\alpha\beta}$ is the meniscus surface area. It is of note that only the volume of phase β remains in Eqn (43); the volume of phase α (which can extend outside the crack limits) is already of no significance.

The potential J_r yields the work of a process under the condition that temperature, mass and loading of the solid and the external pressure and chemical potentials of mobile components are constant. Applying this potential to the process of the crack propagation, we have

$$\mathrm{d}J_r = \mathrm{d}J_r^s + (p^\alpha - p^\beta)\mathrm{d}V^\beta + \sigma^\alpha \mathrm{d}A^\alpha + \sigma^\beta \mathrm{d}A^\beta + \gamma\,\mathrm{d}A^{\alpha\beta} + \mathrm{d}(\kappa L)$$

In this process, an external loading and the corresponding state of the bulk phase of the solid do not change. The only object of change is a complex stress state near the crack, which can be characterized by an excess value $\bar{J}_r^s = wL$ on the side of the solid bulk phase where w is the corresponding work per unit length of the crack front line. Putting $\mathrm{d}J_r^s = \mathrm{d}\bar{J}_r^s$ and assuming the crack to be rectilinear for the sake of simplicity (then the crack length L does not change in the course of the crack growth), we arrive at the expression

$$\mathrm{d}J_r = (p^\alpha - p^\beta)\mathrm{d}V^\beta + \sigma^\alpha \mathrm{d}A^\alpha + \sigma^\beta \mathrm{d}A^\beta + \gamma \mathrm{d}A^{\alpha\beta} + L\mathrm{d}(\kappa + w) \qquad (44)$$

Introducing the total area of the crack walls

$$A = A^\alpha + A^\beta$$

and replacing the pressure difference by γ/r according to the Laplace equation transforms Eqn (44) to

$$\mathrm{d}J_r = \frac{\gamma}{r}\mathrm{d}V^\beta - (\sigma^\alpha - \sigma^\beta)\mathrm{d}A^\beta + \gamma \mathrm{d}A^{\alpha\beta} + \sigma^\alpha \mathrm{d}A + L\mathrm{d}(\kappa + w) \qquad (45)$$

Since the crack depth c is the main parameter of the crack growth, we choose it as a principal independent variable. We also simplify Eqn (45) by dividing it by the constant L. This results in

$$\frac{\mathrm{d}J_r}{\mathrm{d}c} = \frac{\gamma}{r}\frac{\mathrm{d}V^\beta}{\mathrm{d}c} - (\sigma^\alpha - \sigma^\beta)\frac{\mathrm{d}A^\beta}{\mathrm{d}c} + \gamma\frac{\mathrm{d}A^{\alpha\beta}}{\mathrm{d}c} + \sigma^\alpha\frac{\mathrm{d}A}{\mathrm{d}c} + \frac{\mathrm{d}\kappa}{\mathrm{d}c} + \frac{\mathrm{d}w}{\mathrm{d}c} \qquad (46)$$

where all extensive quantities are taken per unit length of the crack front line (V^β now has the dimensions of area whereas A^β, $A^{\alpha\beta}$ and A have the dimensions of length). Geometrically, they are given by the expressions

$$V^\beta = r^2\left(\frac{\cos^2\theta}{\mathrm{tg}\phi} - \sin\theta\cos\theta - \frac{\pi}{2} + \theta + \phi\right) \qquad (47)$$

$$A^\beta = 2r\left(\frac{\cos^2\theta}{\mathrm{tg}\phi} - \sin\theta\right)$$

$$A^{\alpha\beta} = 2r\left(\frac{\pi}{2} - \theta - \phi\right)$$

$$A = \frac{2c}{\cos\phi}$$

where θ is the contact angle for the case of capillary condensation (θ is replaced by $\pi - \theta$ in the case of capillary evaporation).

Equation (46) is the main thermodynamic equation for constructing the theory of strength of materials. To make further steps, we have to adopt a certain mechanism for the crack propagation. The simplest variant is a conformal crack growth when angle ϕ is maintained (not to speak about the constancy of r and θ). Then the quantities V^β, A^β and $A^{\alpha\beta}$ would be be constant and their derivatives in Eqn (46) become zeros. As for the total area of the crack walls, Eqn (47) yields

$$\frac{\mathrm{d}A}{\mathrm{d}c} = \frac{2c}{\cos\phi}$$

It is typical for the conformal growth of a rectilinear crack that thermodynamic line tension κ is dependent on the crack depth c only at the nanoscale and shortly takes a constant macroscopic value for a given angle ϕ.[35] For this reason, for a sufficiently developed crack, we can set that

$$\frac{\mathrm{d}\kappa}{\mathrm{d}c} = 0$$

(the crack under consideration just belongs to this category because it contains a meniscus). Then Eqn (46) takes the form

$$\left(\frac{\mathrm{d}J_r}{\mathrm{d}c}\right)_\phi = \frac{2\sigma^\alpha}{\cos\phi} + \frac{\mathrm{d}w}{\mathrm{d}c} \qquad (48)$$

Since there is no contact angle θ in this relationship, Eqn (48) is equally applicable to the cases of capillary condensation and capillary evaporation.

After substituting Eqn (29) in Eqn (48), we have

$$\left(\frac{\mathrm{d}J_r}{\mathrm{d}c}\right)_\phi = \frac{2\sigma^\alpha}{\cos\phi} - 2bE^2c \qquad (49)$$

Equating the right-hand side of Eqn (49) to zero produces the ultimate strength E_t as

$$E_t = \left(\frac{\sigma^\alpha}{bc\cos\phi}\right)^{1/2} \qquad (50)$$

Differentiating Eqn (49) and substituting Eqn (50) yields

$$\left(\frac{\mathrm{d}^2J_r}{\mathrm{d}c^2}\right)_\phi = -\frac{2\sigma^\alpha}{c\cos\phi} < 0 \qquad (51)$$

Inequality (51) defines the type of extremum of the thermodynamic potential J_r (on passing to an unstable state and the failure of a material), so that the criterion given in Eqn (50) really determines the ultimate strength. Interestingly, of two thermodynamic surface tensions σ^α and σ^β only σ^α appears in Eqn (50), which corresponds to the wider part of the crack. At $\phi = 1$, Eqn (50) changes to Griffith s criterion for an infinitely narrow crack.

We have considered above the case of the conformal growth of a crack as an example. The case of the depth growth of a crack is considerably more complicated. The detailed analysis of that case and the derivation of the ultimate strength can be found in the literature.[36]

VII. Conclusion

Of course, the above consideration is not comprehensive. Chemical thermodynamics is a wide area, and almost each part of it is applicable to materials. For example, such a well known surface property of a material as wetting is of great practical importance and is entirely governed by thermodynamic factors, the thermodynamic surface tension (surface work) σ and the contact angle θ. In this paper, we touched upon the role of these factors in the strength of materials, but wetting has many other interesting aspects. Since σ is physically a scalar quantity, effects related to directions seem to be quite impossible in wetting. The more surprising was the discovery of anisotropy of wetting, the dependence of the contact angle of a wetting liquid on the direction on a solid surface.[37, 38] This phenomenon refers to materials with low elasticity modulus like rubber and typically to elastic polymers (elastomers) for which wetting is accompanied by visible strain. Correspondingly, the explanation of the phenomenon is based on the theory of wetting deformable bodies.[39–44] To induce the anisotropy of wetting, a sheet of rubber should be stretched to cause the orientation of long-chain molecules along the direction of stretching. This makes the sheet anisotropic so that placing a liquid drop on the sheet is accompanied by different works at the three-phase contact lines parallel and perpendicular to the direction of stretching. As a result, the contact angle becomes smaller in the direction of stretching.

Dealing with nanomaterials, a great attention is also paid to nanothermodynamics, which was already reviewed by the author.[3] Among nanomaterials, a special interest is related to newly discovered two-dimensional solids: graphene, silicene and germanene. The thermodynamics of such materials was recently formulated by example of graphene.[45] It is also worthy to say about the thermodynamics of phase transitions. This field became attractive for material scientists long ago[46] and now affiliates to the thermodynamics of nanomaterials in constructing the theory of growth of nanoparticles.[47] However, it holds great promise for extension of thermodynamic theory taking into account the influence of anisotropy of chemical potential on the process of phase transition in a non-hydrostatic stress field.

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