My Discoveries (A Review)

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Abstract—The author gives an overview of his discoveries along the lines of new laws and new phenomena. Included are the following sections: explanation of atmospheric phenomena, such as the occurrence of atmospheric electricity and the presence of precipitation at low supersaturation of water vapor in the atmosphere; development of classical laws of thermodynamics (Laplace, Young and Kelvin equations, phase rules, Gibbs adsorption equations and laws of Konovalov), consideration of nano-corrections to the Gibbs–Curie principle and the Gibbs phase equilibrium condition for a soluble solid particle. Section of new phenomena open surface properties of water and wetting anisotropy. A significant part of the review is the section "Mechanochemistry: laws and new phenomena." Here the tensors of chemical potential and chemical affinity are characterized, the mechanochemical effects of dissolution and stress corrosion, mechanochemical effects in redox reactions involving iron and the mechanochemical effect sign of deformation in wetting phenomena are described. The theme of new phenomena is continued by the strong dependence of the contact angle on the pressure in the liquid and the temperature pinning of the contact angle. The final part tells about the discovery of a new thermodynamic potential, called the J-potential. The necessity of introducing such a potential is manifested in the thermodynamics of solid or mixed systems subjected to complex mechanical stresses. Three applications are demonstrated for J-potential: in the derivation of the classical Gibbs and Neumann equations, in the thermodynamics of thin films and in the theory of strength of materials.

Keywords: nucleation, wetting, dissolution, corrosion, chemical potential tensor, mechanochemistry, J-potential, strength of materials, nanoscience

Science is the most important, the most beautiful and necessary in a man's life, it has always been and will be the highest manifestation of love, only with it alone man will conquer nature and himself.

A.P. Chekhov

1. INTRODUCTION

Science and technics (technology in chemistry) are things different but closely related. Scientists do science, they make discoveries and are advanced team of researchers. Engineers are engaged in technology. They

are thinking about using discoveries for the benefit of mankind and make inventions. During the time of Peter I and Lomonosov, crafts were called arts (Lomonosov considered metallurgy as the most important of the arts). Therefore, with creation of the Russian Academy of Sciences and Arts, Peter I shrewdly expected that the simultaneous going to the academy of scientists and engineers will be a favorable background for the development of science. But he distinguished between these categories of members of the academy: significantly higher payments were made to scientists, than to "artists." This difference would quickly disappeared over time. Science has never been and never will be understandable neither to ordinary people, nor to journalists, nor to power structures. Often it is the technique that is taken for science, and, therefore, holding such a graduation within the academy became unrealistic.

In Soviet times, there was no difference between scientists and engineers as members of the Academy of Sciences of the USSR (on the contrary, the category of administrators imperceptibly increased, which now is especially intensified after the forcible introduction of physicians and agricultural workers in the Russian Academy of Sciences). On the contrary, the difference between discovery and invention was colossal. For an ordinary invention (we will not discuss patenting issues here), it was a fee of 150 rubles (how can we not remember the toilet here, pasted over with copyright certificates, in the Soviet film "Genius!"). The payout for a discovery was incomparably large and amounted to several thousand rubles. Even more important was the halo of glory and honor that surrounded every discovery. Becoming an author of a discovery with receiving the corresponding certificate from the Institute of Patent Examination was the dream of every Soviet scientist.

But let us see if it is really necessary to register discoveries. If an invention is something new, invented by man, then a discovery (like the discovery of America) is what is always was, but was invisible and unknown. To make a discovery, you need to be very careful and thoughtful, not to mention that you just need know a lot. A thousand scientists may pass by some fact and not notice it, and the thousand and one will notice. But if he does not notice, he will have someone to follow, for if anything is really exists, it will be discovered sooner or later. The destiny of discoveries and inventions is completely different. If the discovery is reported immediately and how broadly as possible, the invention is kept secret for the time being. The discovery priority is determined by the date of the first publication. In this way, when a scientist applied for a discovery, he already was definitely its author. Only unresolved the question is whether it is possible to qualify an established new scientific fact as a discovery.

Here we come to the well-known position that not every novelty is a discovery, although every scientific publication must have novelty. A discovery on the empty place should correspond to hold something fundamental and very important new to science. A discovery in some developed department of knowledge should turn over the known conceptions. All this was to be assessed by an expert, and, you see, subjectivism is not due to run. In the late 80s, we applied for registration of the discovery of wetting anisotropy (more on this below) and received a negative review prepared by the V.A. Kabanov's chair at the Moscow State University. After my meeting with him at the chair and the clarifications made, the review was changed to positive. I am afraid to make a mistake, but by then, discoveries were being registered only in three countries (except the USSR, I still remember in Spain and Mongolia). In the rest of the world such registration was considered a pointless bureaucratic procedure. I then (since 1989) was a People's Deputy of the USSR and submitted to the Council of Ministers of the USSR memorandum with a proposal order to stop the registration of discoveries. The corresponding decision was made. In this way, not in Russia, but still in the USSR, a decision was made on the termination of the registration of discoveries.

This was a blow to the scientific bureaucracy, now incredibly expanded. Now to calculate salaries, the value of publications is estimated from power of scientometrics, but the discovery in it is not even mentioned. The value of an article is not determined by its content, but by the journal in which it is published. But the inalienable right of the author is decide where to publish. There was a time when President RAS Yu.S. Osipov urged to publish in domestic journals. Now the situation different, and when I even ask my associates to publish something in a Russian journal, they answer that they are afraid of losing their salary. Returning to discoveries, I want to note that there is a journal for publishing discoveries in Russia. These are Doklady (Reports) of the Russian Academy of Sciences. At least that was for sure in the "Physical Chemistry" section, where I, for many years, was (together with academician I.I. Moiseev) member of

the editorial board. Although this circumstance and the role of Doklaly could be taken into account in the Russian scientometrics to make it more active and fair.

Patent experts believe that there are two kinds of discoveries: the discovery of new laws and discovery of new phenomena. As you know, the most general laws are established by thermodynamics. At 19 century it was the central and most fashionable science, but now has lost its brilliance, although nobody canceled its meaning. Now to engage in thermodynamics is dishonorable and archaic, but a true connoisseur in thermodynamics is extremely difficult to be found. In the region of surface phenomena, among my peers in the world, such specialists could be count on fingers, and almost all of them were my friends. And my personal property to this elite group of scientists was due the fact that I myself was a product of the St. Petersburg thermodynamic school (headed by A.V. Storonkin in my time). I would call this school great and comparable in the world only with the van der Waals thermodynamic school in Holland (for more details, see [1, 2]). My qualification turned into a kind of curse because the ability to see thermodynamic mistakes at first sight often lead to spoilage human relations with proud authors, who did not attach much importance to thermodynamics. Or, even worse, I had to fix the mistakes of our great scientists of the past (such as academicians A.N. Frumkin [3] and B.V. Derjaguin [4]), I wrote that I "execute myself" by doing this.

And what about the classics, Gibbs and van der Waals, did they have any mistakes? There is a famous legend about Gibbs as a scientist without a single mistake, and this is almost truth. Having studied Gibbs up and down (we are talking about his famous work "On the equilibrium of heterogeneous substances"), I found only one error in the section on the elasticity of liquid films [5]. The creator of the only correct chemical thermodynamics really worked practically without mistakes. As for van der Waals' errors, I did not specifically deal with them, but noticed the presence of an error associated with an excluded volume in the equation of state [6]. Well, am I myself absolutely sinless? If! I think about a dozen errors in publications (the number of my publications approaches 800), but all of them are fixed by now. The fact is that my mistakes do not strike the eye, but are visible to me, so, in basically, I found them myself. There was only one exception, when my mistake was found by our common with F.M. Kuni postgraduate student A.K. Shchekin (now Corresponding Member of the Russian Academy of Sciences), which required to reformulate the foundations of nucleation thermodynamics on charged centers [7].

It should be noted here that errors can be different. It is one thing to make a mistake due to inattention and still beyond the principles, and another thing is to repeat rippling frontal attacks on Gibbs' thermodynamics. Homegrown "geniuses" create their own variants of thermodynamics and exhibit a greater inventiveness in their defense. Butler [8] was one of the first, whose theory (with rigid adsorption layer) was quite slender, but incompatible with Gibbs' thermodynamics. A.A. Zhukhovitsky was Butler's follower in the USSR [9, 10], whose school is still operating. But there are other followers of Butler in the world, against which I had to speak. My criticism [11] was published in the Journal of Physical Chemistry along with a short answer by the authors of type "the fool himself" without delving into my arguments [12]. Outraged J.C. Ericsson (Sweden), one of the world leaders in thermodynamics, tried to intervene in this story, but the editor-in-chief of the journal answered him: the both points of view are published, a reader will decide for himself which of them is right. A very weak position! Only a completed discussion would be useful to the reader. Here's a contrasting example: paired with the same Ericsson, we fought for Gibbs' thermodynamics versus some kind of "Hermann's thermodynamics" in a grueling discussion with a group of Western scientists on the pages of the journal Surface Science (I provide a link only to our first article in this series [13]). The discussion went to its logical conclusion, and, I think, was very instructive for readers. I have brought only two examples, but they were many. The protection of Gibbs' authentic chemical thermodynamics was a noble cause throughout my life and remains so today [14] (now together with my pupils, which makes me happy).

Since the vast majority of my researches is of a thermodynamic nature, they are so or otherwise associated with the discovery of new laws. In thermodynamics of surface phenomena, it is difficult to find a pattern that would not be subjected to clarification by my efforts. But the clarification of something already discovered can hardly be considered as a new discovery, although everything depends on the significance of the clarification. In this part, below will be presented only the most significant results. With another hand, thermodynamic work can pretell new phenomena and stimulate their real discovery. This has happened more than once and will be

also presented below. The discovery of new phenomena often happens by chance, and not every experimentalist can immediately understand what he has done. It was repeatedly that I had to explain to people what they discovered, create a theory of a new phenomenon and put new experiments for its better disclosure. Thus, I became a full-fledged participant of the discovery team. It will be nice to present similar discoveries below.

Finally, another type of important or even the most important works related to the explanation of phenomena observed by mankind from time immemorial. On a historical scale, experiment was introduced into science (through the efforts of Galileo and other pioneers) relatively recently. Before scientists simply observed nature and generalized their observations within the framework of natural philosophy (remember the 8-volume physics of Aristotle). But there are grandiose phenomena such as atmospheric electricity, which even after that remained just to observe, and, of course, try to clarify. If for millennia there was no strict explanation of this phenomenon, and we succeeded, then it is something. This is where I will start.

2. EXPLANATION OF ATMOSPHERIC PHENOMENA

Once I was walking with a participant in many experiments with clouds, an outstanding professor of meteorology V.G. Morachevsky, and pointing to a large cloud, he asked: "How much water do you think is in it?" I answered at random: "I think more than a ton," and was immediately corrected and stunned: "There are a hundred thousand tons of water in this cloud." Yes, reader, we are invading the scientific field, where everything is grandiose and the gigantic forces of nature demonstrate their power. Atmospheric electricity forms a particularly clear and impressive picture.

2.1. Atmospheric Electricity

Of course, humanity has been thinking about thunder and lightning throughout its history, but it became possible to talk about atmospheric electricity only after the discovery of electricity itself, i.e. after 1800, when the world's first battery,"voltaic pile," appeared. The "age of electricity" that followed was marked by an incredible number of important discoveries and inventions, which finally led to the discussion of atmospheric electricity with the creation of more than a dozen theories and the involvement of prominent physicists and Nobelists in

the discussion. I will quote two of them. The first one, the discoverer of the electron, Joseph Thomson, believed that if it was possible to prove that an external electric field affects the surface tension of water with its sign (he himself failed in this), then the origin of atmospheric electricity would be explained [15] (looking ahead, I note that this is exactly what we managed to do). Thomson proceeded from the fact that when water condenses on atmospheric ions, a drop is formed with a charge in the center; therefore, the surface of the drop is in the electric field.

Another Nobelist, one of the founders of quantum electrodynamics, Richard Feynman, in his famous course of theoretical physics (published in our country in the 60s in the form of a 9-volume series of "Feynman Lectures on Physics") singled out a whole chapter on the problem of atmospheric electricity [16]. Unlike Thomson, Feynman did not put the problem of nucleation at the forefront and considered the discovery of cosmic rays to be the most important in this area. He analyzed the ascending and descending currents of air and water vapor, taking into account many transient factors. It is quite impressive that Feynman explained the sudden onset of a cold wind before a thunderstorm. However, some facts were taken from the experiment and simply used as a given. The most important of these are the negative charge of the Earth, the polarization of the clouds in spite of this (with a positive charge at the top and a negative charge at the bottom), and the predominantly negative charge of rain. Obviously, the latter follows from the penultimate one, and the negative charge of rain contributes to the negative charge of the Earth. But Feynman believed that the charge of the Earth is formed by lightning (during a thunderstorm, the difference in electrical potentials between the lower part of the cloud and the Earth reaches one hundred million volts). One can argue here: about 300 thunderstorms occur on Earth every year, and there are an innumerable number of simple rains. However, it does not matter, because both factors work in the same direction. As regards the separation of charges in a cloud, Feynman cited two explanations available in the literature and criticized them. In essence, he sharpened the problem, but did not solve it. The question remains: what kind of gigantic power is this machine that, despite the charge of the Earth (creating a potential gradient of 100 V/m near its surface), separates the charges in the cloud?

For further progress, it was necessary to develop the theory of nucleation (condensation) of water on charged

centers, taking into account the surface potential of water. This value, denoted as $\Delta\varphi_0$ represents a jump in the electric potential during the transition from air to water and is due to the spontaneous orientation of the dipoles of water molecules on its surface (the subscript "zero" indicates the absence of an external electric field). There have been talks about $\Delta\varphi_0$ for a long time. Frenkel considered it to be the result of dipole-quadrupole interaction [17, p. 329], and the head of our (we can safely add the world) electrochemistry A.N. Frumkin determined it experimentally as + 0.1 V [18], i.e. with a positive sign. However, even with regard to the sign of the water potential, there was wide disagreement in the world. To overcome it, we (I mean the staff of the Laboratory of Surface Phenomena of the Faculty of Chemistry of Leningrad State University) chose to measure the potential on a water jet, i.e. under dynamic conditions, clearly showing in which direction the sign of the potential changes when equilibrium is established. Surprisingly, the obtained the result + 0.1 V exactly coinciding with the result of [18]. This pleased A.N. Frumkin, and he submitted our paper to Doklady [19], but said that he would have done it even if the sign of our potential turned out to be opposite. Thus, the dispute about the sign of the surface potential of water was resolved.

Inspired, I rushed to formulate the thermodynamics of water condensation on charged centers, published a series of articles here and abroad, and, it seems, explained everything. This was sympathetically observed by my friend and classmate in the Faculty of Physics, the outstanding theoretical physicist F.M. Kuni (a student of Academician V.A. Fock, who explained to me in his student years that the difference between an Academician and a professor is the same as between a professor and a student). In view of the importance of the topic, we decided to continue it by taking a joint postgraduate student. It turned out to be A.K. Shchekin, and the reader already knows the rest from the introduction: my whole theory went into the wastebasket. Instead, publications appeared that corrected the situation [7, 20] and developed the theory further [21–25].

History is very instructive, because in order to give a correct theory, it was necessary to go through one more discovery that overturned the existing ideas. Let me explain this in more detail. Applying thermodynamics to solids, Gibbs discovered the dualism of surface tension, which consists in the fact that the thermodynamic
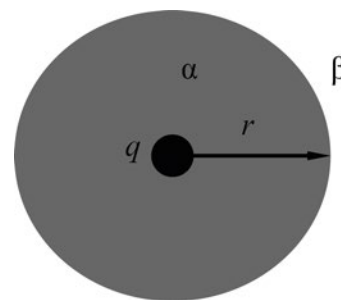

Fig. 1. A drop of liquid α of radius r with a central charge q in a gas-vapor mixture β.

definition of surface tension as the work of formation of a unit of a new surface (Gibbs' own designation σ) and the mechanical definition as surface force per unit length (our designation γ) lead to different σ ≠ γ. At the same time, for liquids, as it was believed, always σ = γ. So it turns out not always, as evidenced by the formula for a spherical drop with a charge in the center [7, 20]

$$\sigma = \gamma - \mathsf{P}D, \tag{1}$$

where P is the excess surface polarization of the drop and D is the electric induction (for a spherical drop of radius r with a central charge q we have $D = q/r^2$). At one time this was not noted, but now I state that Eq. (1) is a discovery. The discovery of the dualism of surface tension for liquids in an electric field, which turned the then prevailing ideas (on the basis of which the first version of the theory was created). Taking into account Eq. (1), both the surface tensions can be monitored in theory, but, on the other hand, any ratio can be expressed in terms of either σ or γ. I note that in these works the electric field is directed along the normal to the surface of the liquid. The general case of an arbitrary direction of the electric field towards the liquid surface was considered in [26].

Let us now turn directly to the results of [20–25]. The object of consideration is a drop of radius r with a bulk phase α and a central charge q, located in the gas phase β (Fig. 1). In a spherically symmetric system, the radial direction is considered positive, so now we will estimate the jump in the electric potential during the transition from the liquid phase to the gas phase (in particular, for water, one should write $\Delta\varphi_0 = -0.1$ V). Surface polarization can be written as [22]

$$\mathsf{P} = \mathsf{P}_0 + k_1 \frac{q}{r^2} + k_2 \frac{q^2}{r^4}, \tag{2}$$

where $P_0 = 4\pi\Delta\varphi_0$ is the spontaneous surface polarization in the absence of an external electric field and r is the droplet radius. The coefficients of linear and quadratic polarizability of the surface layer were estimated as

$$k_1 \sim \frac{1}{4\pi}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{\Gamma_\infty}{\rho_\infty^\alpha}, \quad k_2 \sim -\frac{\kappa}{4\pi\rho_\infty^\alpha}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{P_{0\infty}}{k_B T}. \quad (3)$$

where ε is the permittivity, ρ is the number of molecules per unit volume, Γ is the adsorption of the condensate, the indices α and β refer to the liquid and, respectively, to the gas phases, the subscript ∞ marks the quantities related to the flat liquid-vapor interface in the absence of an electric field, the numerical factor κ depends on the nature of the condensate ($\kappa \sim 1.4$ for water).

The expression for the work of drop formation has the form [7, 20, 22, 23]

$$W = \frac{4\pi}{3}\gamma_\infty r^2(1 - 2\delta_1 - 6\delta_5) - 4\pi P_{0\infty}q$$
$$+ \frac{2q^2}{3r^4}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\left(1 + \frac{1}{4}\delta_1 - \frac{5}{4}\delta_4 + \frac{3}{4}\delta_5 - \frac{7}{6}\delta_6\right) + \Omega_n, \quad (4)$$

where Ω_n is the minimum work of ion transfer from the gas phase to the liquid phase. Small parameters are given by expressions

$$\delta_1 \equiv \frac{\Gamma_\infty}{\rho_\infty^\alpha r}, \quad \delta_4 \equiv 8\pi k_1\Big/\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)r,$$
$$\delta_5 \equiv q\Big/\left(\frac{dP_0}{d\mu}\right)_\infty \rho_\infty^\alpha r^3, \quad \delta_6 \equiv -\frac{qP_{0\infty}}{\rho_\infty^\alpha kTr^3}, \quad (5)$$

where μ is the chemical potential of liquid molecules. In Eq. (4) there are linear in charge terms $-4\pi P_{0\infty}q$, $8\pi\gamma_\infty r^2\delta_5$ and Ω_n, which were so lacking for J. Thomson. It would seem that their presence should also be preserved in the expression for the nucleation rate, which is proportional to $\exp(-W/kT)$ in the case of homogeneous nucleation. However, in contrast to homogeneous nucleation in supersaturated vapor, condensation of droplets around ions occurs even in unsaturated vapor. This means that the work W of drop formation on an ion has not only a maximum $W(r_{max})$ at a certain radius $r = r_{max}$, but also a minimum $W(r_{min})$ with a negative value of W at $r = r_{min}$. In this case, the nucleation rate is set not by the work of nucleus formation, but by the activation barrier of nucleation ΔW, which is determined as the difference between the indicated values:

$$\Delta W = W(r_{max}) - W(r_{min}), \quad (6)$$

and will be proportional to $\exp(-W/kT)$. In this case, all the above terms linear in charge are eliminated.

To reveal the effect of the sign of the charge, the expression for the chemical potential of the condensate is more useful and clear [22]

$$\mu = \mu_\infty + \frac{2\gamma_\infty}{\rho_\infty^\alpha r}\left(1 - 2\delta_1 - \frac{1}{2}\delta_2\right)$$
$$- \frac{q^2}{8\pi\rho_\infty^\alpha r^4}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\left(1 - 2(\delta_1 + \delta_4) - \delta_2 + \frac{1}{2}\delta_3 - \frac{8}{3}\delta_6\right), \quad (7)$$

in which, in comparison with Eq. (4), the parameters are added

$$\delta_2 \equiv \frac{2\chi_\infty\gamma_\infty}{r}, \quad \delta_3 \equiv \chi_\infty\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)q^2\Big/8\pi r^4, \quad (8)$$

where χ is the compressibility of the liquid phase. Let us now compare the chemical potentials μ^+ and μ^- of liquid molecules in drops of the same size, but with charges opposite in sign. For their difference from Eq. (7) we obtain in the leading order

$$\mu^+ - \mu^- = \frac{8}{3}\frac{|q|^3 k_2}{\rho_\infty^\alpha r^7} \approx -\frac{8}{3}\frac{\kappa|q|^3}{4\pi(\rho_\infty^\alpha)^2 r^7}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{P_{0\infty}}{kT}$$
$$= -\frac{8}{3}\frac{\kappa|q|^3}{(\rho_\infty^\alpha)^2 r^7}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{\Delta\varphi_0}{kT}. \quad (9)$$

The sign of the right side of Eq. (9) is opposite to the sign of $\Delta\varphi_0$. For water $\Delta\varphi_0 = -0.1$ V, and, consequently, the right side of Eq. (9) is positive, i.e. the chemical potential of molecules in a drop with a positive charge is higher than in a drop with a negative charge. Substance always moves from places of higher chemical potential to places of lower chemical potential. This means that if identical drops of water were randomly formed on ions of different signs, then the pumping of water from a positively charged to a negatively charged drop would immediately begin. In other words, under normal (equilibrium) conditions, negatively charged droplets should be larger than positively charged ones. Larger means heavier, and then the gravitational field carries

negatively charged drops to the lower part of the cloud, which explains the separation of charges. Thus, Eq. (10) makes it possible to explain the separation of charges in a cloud.

The whole process of charge separation can be traced as follows. Due to the ionizing action of cosmic rays, the atmosphere always contains a diverse set of free ions and other charged particles. In the presence of water vapor, they all become condensation centers. Due to the existence of the surface potential of water, droplets on negatively charged centers grow faster and become larger and heavier than positively charged droplets. Then the gravitational field of the Earth, overcoming the polarizing effect of its own charge, transfers negatively charged drops to the lower part of the cloud. Negatively charged rain pours from it and lightning strikes, giving our planet a negative charge. From this explanation, it is clear that the mysterious super-powerful machine that separates charges in the atmosphere is nothing but the Earth's gravitational field.

2.2. Precipitation at Low Supersaturation of Water Vapor in the Atmosphere

In addition to the origin of atmospheric electricity, there are other mysteries in meteorology. The most important of them strikes with the simplicity of the question: why is it raining? Rain is a phase process (water condensation), which requires a certain degree of supersaturation of the parent phase (water vapor) for its implementation, i.e. so that the partial pressure of water vapor p or the chemical potential of vapor μ are respectively higher than the equilibrium values p_∞ and μ_∞ for a flat surface. The degree of supersaturation $\zeta \equiv (p - p_\infty)/p_\infty$ and the chemical potential are related by the relationship

$$\mu - \mu_\infty = \kappa T \ln(1 + \zeta). \tag{10}$$

According to experiments with a cloud chamber, the condensation of water even on ions requires a 4.5-fold supersaturation (an 8-fold supersaturation is required for a purely homogeneous condensation). There is no such degree of supersaturation in clouds. Water condensation occurs at an insignificant degree of supersaturation (say, $\zeta = 0.02$), i.e. almost barrier-free (according to (10), at small ζ, the chemical potential measured in units of kT from is also small). It would seem that there should not be any rain, but it is. Where does such a miracle come from?
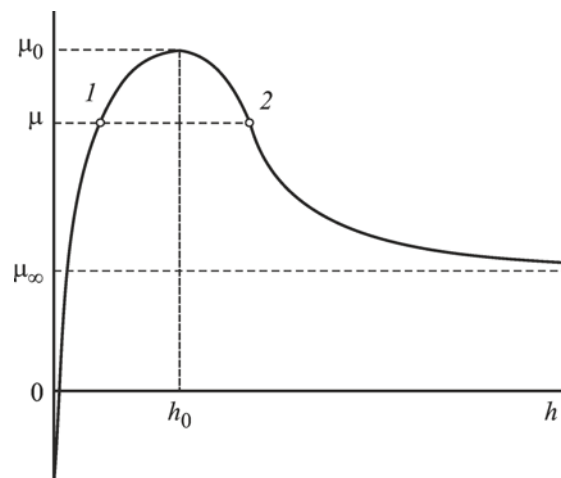

Fig. 2. Dependence of the chemical potential μ on the thickness of the germ film of water h on the insoluble core. Points *1* and *2* correspond to a stable and unstable germ, respectively.

To better explain the problem, let us see how the chemical potential of water changes as the condensate film thickens on a spherical wetted particle [27, 28]. On Fig. 2 μ is the chemical potential of water molecules in the film and h is the film thickness, μ_∞ is the value of μ in an equilibrium macroscopic water-vapor system with a flat interfacial surface. This state corresponds to saturation, and supersaturation corresponds to the difference $\mu_0 - \mu_\infty > 0$. Consider the dependence of the chemical potential on the thickness of the condensate film. In the region of small h and undersaturation $\mu - \mu_\infty < 0$, we obviously have according to the laws of adsorption: the higher the chemical potential, the thicker the adsorption film. In the region of large h, the macroscopic drop must obey the Kelvin equation (we will return to it later), according to which (taking into account the fact that the drop radius also increases with the film thickness) $d\mu/dh < 0$. An increase at small and a decrease at large h means the presence of a maximum of the chemical potential at some value μ_0 (Fig. 2). The difference corresponds to the limiting (we will say "threshold," because the word "limiting" is usually associated with the spinodal) supersaturation, above which the energy barrier of nucleation disappears, and water condensation occurs freely. Below, each value of the chemical potential corresponds to two nuclei: stable (point *1*), which is formed spontaneously without the expenditure of work, and unstable (point *2*), the transition to which requires work, called the energy barrier of nucleation. In the previous section, we encountered such a situation

for drops on charged nuclei. Now we see that it is characteristic of any condensation nuclei, not necessarily charged ones.

It is clear from the consideration that if we find the reason why the limiting supersaturation of water in the atmosphere can actually become very small, then we will explain the existence of rain. The thermodynamic theory also solved this problem, and it turned out that two independent mechanisms can lead to ultralow limiting supersaturation. The first is disjoining pressure (a term from colloid science associated with the play of molecular forces in a thin film) during the formation of a thin film nucleus on a wetted core (most often silicate sand particles originating from numerous deserts). The second mechanism is the dissolution of the nucleus itself during the formation of the nucleus (the role of such nuclei is played by salt particles formed in the atmosphere when ocean spray dries up). Let us consider both mechanisms separately.

Disjoining pressure. In the 1930s, B.V. Deryagin discovered one of the most important quantities of colloidal science, the disjoining pressure of thin films Π. One of his definitions reads [29]

$$\Pi \equiv p^{\beta} - p^{\alpha}, \qquad (11)$$

where p^{α} is the pressure in the equilibrium mother bulk phase α of a thin film at the same temperature and chemical potentials as in the film, and p^{β} is the external pressure on the film. Equation (11) implies that the film is flat. When passing to a spherical film of radius r, the relation [30, p. 70]

$$p^{\alpha} - p^{\beta} = \frac{2\gamma_{\infty}}{r} - \Pi(h), \qquad (12)$$

where the first term on the right hand side is the Laplace capillary pressure (we will talk about it in more detail in another section). The value γ_{∞} is the surface tension of a macroscopic drop (at $r = \infty$). It should be noted that the concept of disjoining pressure, like the phenomenon itself, is beyond the scope of Gibbs chemical thermodynamics. The task of introducing disjoining pressure into the thermodynamic apparatus and determining its place in chemical thermodynamics fell to my lot [31, 32].

Let us now show how to build a quantitative theory for a one-component germ in the form of a liquid film on the nucleus [27, 28]. Under isothermal conditions, the Gibbs-Duhem equation for the phase α is simplified to the form

$$d\mu^{\alpha} = v^{\alpha} dp^{\alpha}, \qquad (13)$$

where v^{α} is the molecular volume of the liquid, which is practically constant far from the critical point. The integration of Eq. (13) gives

$$\mu^{\alpha} - \mu_{\infty}^{\alpha} = v^{\alpha}(p^{\alpha} - p_{\infty}^{\alpha}). \qquad (14)$$

Substituting Eq. (12) into Eq. (14), taking into account the equality of phase pressure p^{α}_{∞} and p^{β}_{∞} and the constancy of the external pressure p^{β} (due to the presence of air in the atmosphere), leads to the relation

$$\mu^{\alpha} - \mu_{\infty}^{\alpha} = v^{\alpha}\left[\frac{2\gamma_{\infty}}{r_n + h} - \Pi(h)\right], \qquad (15)$$

where r_n is the radius of the wetted core (obviously, $r_n + h = r$). Eq. (15) characterizes the dependence $\mu^{\alpha}(h)$ in Fig. 2. True, above we described the ascending branch in adsorption terms (assuming the film of the nucleus to be an adsorption layer), and now (assuming the nucleus to be a thin film) in terms of the disjoining pressure. There are two opposing terms in square brackets, leading to the appearance of a maximum.

Equation (15) can be written as

$$\ln(1 + \zeta) = \frac{v^{\alpha}}{kT}\left[\frac{2\gamma_{\infty}}{r_n + h} - \Pi(h)\right]. \qquad (16)$$

For water films on quartz, the experiment gives a dependence of the form [33]

$$\Pi(h) = K\exp(-h/l), \qquad (17)$$

where K and l are constants. Taking into account Eq. (17), using the experimental values of K and l, from Eq. (16) for a wettable core with a radius of 10 nm, the threshold supersaturation $\zeta_0 \approx 0.1$ was calculated [27]. This confirms the role of the disjoining pressure in the creation of rain at ultra-low supersaturations in the atmosphere.

Soluble condensation nuclei. Let us now complicate the problem by assuming that the core is soluble. Then the nucleus will be not just a liquid film, but a film of a solution of the substance of the core, and Eq. (15) is replaced by the expression [34]

$$b = -x + \frac{2\gamma_{\infty}v^{\alpha}}{kTr} - \frac{v^{\alpha}\Pi}{kT}, \qquad (18)$$

where $b \equiv (\mu - \mu_\infty)/kT$, x is the mole fraction of the core substance in the solution and is the partial molar volume of water in the solution. Figure 3 illustrates the situation for the soluble core graphically. The difference $r - r_n$ is taken as an independent variable. Until the core is dissolved, this difference is the thickness h of the film of the nucleus, and, after the complete dissolution of the core ($r_n = 0$), the radius of the drop of the solution of the substance of the nucleus. The dotted line shows the contributions of individual terms in Eq. (18). Of particular interest is the contribution from the solubility of the nucleus. It can be seen that the dependence $b(h)$ in the presence of the nucleus even differs qualitatively (in the sign of the derivative) from the dependence $b(r)$ in the case of complete dissolution of the core. It is also interesting that there are two maxima in b (in fact, it was discovered in [34] that the threshold supersaturation may not be the only one).

Using a formula like Eq. (17), in [34], numerical estimates of threshold supersaturations were carried out in the presence of cores of NaCl, Na_2SO_4, and $CaSO_4$ salts with decreasing solubility at a temperature of 271 K. All of them indicate that the threshold supersaturation is small. For example, for the original $CaSO_4$ core containing 125000 undissociated molecules, 0.13 was obtained. The values we are talking about now correspond to the left maximum in Fig. 3. The theory is constructed similarly for the right maximum, when the core has completely dissolved and now exerts its influence through a fixed amount of the substance of the core present in the solution drop [35, 36]. The behavior of surfactant cores, the effect of adsorption layers, and many other nuances for soluble cores can be found in [37–40].

Finally, concluding the section related to the explanation of atmospheric phenomena, we note the following. As was mentioned above, there are other theories. However, only our theory is built on a thermodynamic basis, which means that it is the most justified. The rigor that comes from thermodynamics cannot be refuted.

3. DEVELOPMENT OF THE CLASSICAL LAWS OF SURFACE PHENOMENA

Everything that was done in the theory of surface phenomena before Gibbs is called the traditional theory of capillarity. In essence, it is formed by the equations of Laplace and Young for surface tension. The outstanding mathematician, mechanic and astronomer Pierre-Simon
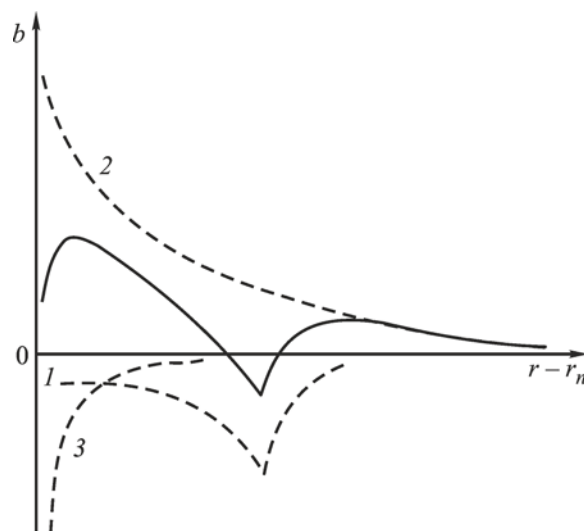

Fig. 3. Dependence of quantity $b \equiv (\mu - \mu_\infty)/kT$ on the difference $r - r_n$ in the case of a soluble core (solid line) according to Eq. (18) [34]. Dashed lines *1*, *2*, and *3* are the contributions of the first, second, and third terms on the right hand side of Eq. (18).

Laplace was 24 years older than Thomas Young, who was almost the same age as Napoleon. Both of them treated Laplace with great reverence. Joung wrote an article about Laplace in the Encyclopædia Britannica, and Napoleon (he was a corresponding member of the Paris Academy of Sciences, where he became close to Laplace) tried to involve him in government activities and even included him in the government for a while. Compared to (the count under Napoleon and the marquis after the restoration) de Laplace, in an embroidered gold uniform with stars, Young looked very modest, and I would characterize him with only one word: genius. Starting to do something from the age of two, at the age of 21 he was elected to the Royal Society as a doctor for his work on the accommodation of the lens of the eye. Later, he explained color vision and made contributions to various fields of science, and not only natural ones. Young's modulus in mechanics, the wave theory of light, that's all he is, but how do you like the decoding of Egyptian hieroglyphs! One of Young's obituaries was entitled "The Last Man Who Knew Everything."

Young survived both the great Frenchmen and died in 1829, and 10 years later J.W. Gibbs was born. But, since, unlike Young, Gibbs published at a very mature age, a half-century intermission formed in the development of the theory of capillarity. However, while the theory of
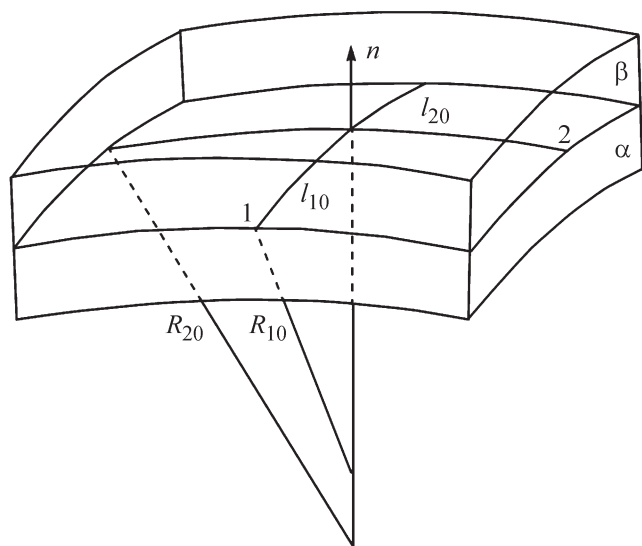
Fig. 4. Element of a non-spherical interface.

capillarity was languishing in anticipation of Gibbs, it was visited by the "king of Victorian physics" William Thomson (the future Lord Kelvin) and left there his famous equation (we will call it the Kelvin equation so as not to be confused with the work of Joseph Thomson) about the vapor pressure of a small drops [41]. In fact, we have already used it in explaining atmospheric phenomena (for example, the second term on the right hand side of Eq. (18) in the previous section). The Kelvin equation is the central relation of the theory of nucleation, and is adjacent to the main laws of the traditional theory of capillarity.

It must be said that during the period of this intermission in the development of the theory of capillarity, thermodynamics itself developed by leaps and bounds. The appearance of Gibbs's work marked the creation of chemical thermodynamics due to the introduction of the chemical potential (the main quantity of chemistry in general). Gibbs published the work already mentioned above "On the Equilibrium of Heterogeneous Substances" in two parts: the first (thermodynamics of heterogeneous systems) in 1876, and the main law here was the phase rule. The second part (1878) was precisely the theory of capillarity, where the Gibbs adsorption equation was the main law. Thus, we have already accumulated five laws. We will start with them, and then add something else.

3.1. The Laplace Equation

The Laplace equation is best known in its simplest classical form

$$p^{\alpha} - p^{\beta} = \frac{2\gamma}{R}, \qquad (19)$$

where p is the hydrostatic pressure, α and β are symbols of contacting phases separated by a spherical surface with tension γ and radius R. Equation (19) is the condition of mechanical equilibrium between two isotropic phases separated by a curved interfacial surface. There have been many attempts to generalize the Laplace equation (we refer the interested reader to the author's reviews [42, 43]). When considering the general case of anisotropic phases, the most complete analogue of the Laplace equation was given in [44, 45], but the relation given there is only one component of the complete condition of mechanical equilibrium on a curved surface. The complete condition of mechanical equilibrium was obtained in [46, 47], and we will dwell on this in more detail.

The most general approach assumes the anisotropy of the mechanical state both in the bulk and on the surface. The mechanical state is specified at each point of the bulk phase by the pressure tensor $\hat{p}$ or, equivalently, by the stress tensor $\hat{E} \equiv -\hat{p}$, and at each point of the surface by the surface tension tensor $\hat{\gamma}$ (not necessarily two-dimensional). In this case, it should be taken into account that the gradient of the surface curvature may be accompanied by a gradient of the surface tension tensor. In addition, the result must be consistent with the general equilibrium condition of continuum mechanics

$$\nabla \cdot \hat{p} = 0, \qquad (20)$$

where ∇ is the vector gradient operator, and $\hat{p}$ is the total pressure tensor (taking into account external fields). Equivalent to Eq. (20), the condition of mechanical equilibrium inside an element of a two-phase system with an interfacial surface (Fig. 4) can be written as

$$-\oint(\hat{p} \cdot d\mathbf{A}) = -\oint \mathbf{P} dA = 0, \qquad (21)$$

where $-\hat{p}$ is the local stress tensor, $d\mathbf{A} = \mathbf{v} dA$ is the element surface differential vector ($\mathbf{v}$ is the unit vector of the outer normal to the surface element, A is the area), $-\mathbf{P} = -\hat{p}\mathbf{v}$ is the force vector applied to the element surface unit (stress vector), integration is carried out over the entire enclosed surface. Detailing Eq. (21) leads to the relation [46, 47]

$$\mathbf{P}_3^{\alpha} - \mathbf{P}_3^{\beta} = -\frac{\partial \gamma_1}{\partial l_{10}} - \frac{\partial \gamma_2}{\partial l_{20}}, \qquad (22)$$

where l_1 and l_2 are the lengths of the coordinate lines in the curvilinear coordinate system, and the additional subscript "zero" indicates that they belong to an arbitrarily chosen dividing surface (to which, of course, the surface tension tensor is related). The designations γ_1 and γ_2 correspond to the force definition of the surface tension vector on the cross sections of the surface layer perpendicular to directions 1 and 2. The physical meaning of γ_1 and γ_2 is that for each of the cross sections of the surface layer, they represent excess stresses on the lines l_{20} and l_{10}, respectively.

Equation (22) surprises with the simplicity that is achieved due to the representation in a vector (not in a tensor) form (how can one not recall Gibbs's saying that each researcher should choose such a point of view so that the subject appears in the greatest simplicity). In terms of compactness, Eq. (22) is in no way inferior to Eq. (19), and in terms of generality, it significantly exceeds both the Laplace equation itself and all its earlier generalizations. In its form and (vector) nature, Eq. (22) differs significantly from the Laplace equation and cannot be called its generalization. Another thing is that the latter can be deduced as one of the consequences of this relation. By the successive scalar multiplication of Eq. (22) by the orts of an orthogonal curvilinear coordinate system using differential geometry, Eq. (22) is detailed by three scalar equalities

$$p_{13}^{\alpha} - p_{13}^{\beta} = -\frac{\gamma_{31}}{R_{10}} - \frac{\partial \gamma_{11}}{\partial l_{10}} - \frac{\partial \gamma_{12}}{\partial l_{20}}, \tag{23}$$

$$p_{23}^{\alpha} - p_{23}^{\beta} = -\frac{\gamma_{32}}{R_{20}} - \frac{\partial \gamma_{21}}{\partial l_{10}} - \frac{\partial \gamma_{22}}{\partial l_{20}}, \tag{24}$$

$$p_{33}^{\alpha} - p_{33}^{\beta} = \frac{\gamma_{11}}{R_{10}} + \frac{\gamma_{22}}{R_{20}} - \frac{\partial \gamma_{31}}{\partial l_{10}} - \frac{\partial \gamma_{32}}{\partial l_{20}}. \tag{25}$$

The last equality is the generalization of the Laplace equation obtained earlier in [44]. In [45, 47], attention was paid to the three-dimensional aspect of surface tension, which is illustrated in Eqs. (23)–(25) by the quantities γ_{31} and γ_{32}. If surface tension were a purely two-dimensional tensor, these components would not exist.

3.2. The Young Equation

The Young equation refers to the phenomenon of incomplete wetting of a solid surface, when the liquid forms a contact angle with it. In its classical form, the Young equation appears as
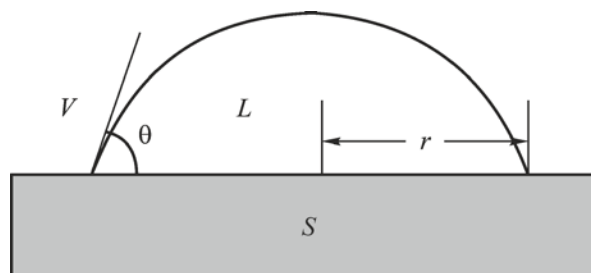

Fig. 5. A drop on the surface of a solid body: θ is the contact angle, r is the radius of the three-phase contact line.

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta, \tag{26}$$

where σ is the thermodynamic (in contrast to the mechanical γ in the Laplace equation) surface tension, θ is the contact angle, the subscripts S, L and V refer to the solid, liquid and gaseous (or second liquid) phases, respectively, and their double combinations refer to the corresponding surfaces (Fig. 5). The development of the Young equation has a long history, and we again refer the reader to reviews [42, 43]. Here we note that the work took place in a number of areas. The first one is related to taking into account the (thermodynamic) linear tension κ, which appears due to the presence of a three-phase contact line. First, an additional term κ/r appeared in the Young equation, where r is the radius of the three-phase contact line, and then (for the first time in [48]) is the derivative $\partial \kappa / \partial r$ at constant temperature and chemical potentials. In the same work, the generalized Young equation was derived, corrected for linear tension [48]

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta + \left(\frac{\kappa}{r} + \frac{\partial \kappa}{\partial r} \right) \cos \varphi, \tag{27}$$

where φ is the angle between the substrate and the local plane of the three-phase contact line (taking into account the relief of the wetted surface). It should be emphasized that the derivative $\partial \kappa / \partial r$ is an important factor in the generalization of the Young equation, and its unmotivated rejection is unacceptable. In particular, this derivative reflects the dependence of surface and linear tensions on the position of the dividing surface (radius R). This can be seen from the relation [49]

$$\frac{\partial \kappa}{\partial r} = \left[\frac{d\kappa}{dr} \right] + \frac{r \, \mathrm{tg}\, \theta}{2} \left[\frac{d\sigma_{LV}}{dR} \right], \tag{28}$$

where direct brackets mark the derivatives corresponding to the mental displacement of the dividing surface.

The second direction in the development of the Young equation is taking into account the roughness and mosaicity of the surface of a solid body and, as a consequence, the roughness of the three-phase contact line. The surface roughness coefficient is defined as

$$k_s \equiv A'_{SV}/A_{SV} = A'_{SL}/A_{SL}, \qquad (29)$$

where A is the visible and A' is the real surface area of the solid (it is assumed that the roughness coefficient does not change upon wetting). Similarly, the line roughness coefficient is introduced

$$k_l \equiv L'/L, \qquad (30)$$

where L is the apparent and L' is the real length of the three-phase contact line, and the line roughness can manifest itself even on a smooth, but microheterogeneous (mosaic) surface. Taking into account these two types of roughness, the generalized Young equation takes the form [42, 50, 51]

$$\cos\theta = k_s \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} - \frac{k_l}{\sigma_{LV}}\left(\frac{\kappa}{r} + \frac{\partial\kappa}{\partial r}\right). \qquad (31)$$

Neglecting the linear tension ($\kappa = 0$), Eq. (31) transforms into the well-known Wenzel equation [52], so that relation (31) is also a generalization of the Wenzel equation.

Another direction in the development of the Young equation is to take into account the deformation of the substrate caused, on the one hand, by the excess Laplace pressure inside the drop, which leads to the punching of the substrate, and, on the other hand, by the surface tension of the drop, which leads to the stretching of the substrate and the formation of a welt along the line of the three-phase contact. In the classical Young equation, such effects are not taken into account, because the wetted body is assumed to be absolutely rigid. But for a rubber type substrate or, even better, a gel, they need to be taken into account. The theory of wetting of elastic bodies was formulated in [48, 51–58]. Since the work of deformation is directly related to the three-phase contact line, it is convenient to include it in the thermodynamic linear tension. Thus, the theory is reduced to calculating

the effective linear tension (which is orders of magnitude higher than the usual linear tension on non-deformable surfaces) as the work of deformation per unit length of the three-phase contact line. Everything else can then be calculated using the generalized Young equation (31).

3.3. The Kelvin Equation

Although, as already noted, the Kelvin equation for the vapor pressure of a drop belongs to pre-Gibbs thermodynamics, it received its full sound (impossible without the concept of chemical potential) in Gibbs thermodynamics. The classical Kelvin equation has the form

$$\ln\frac{p}{p_\infty} = \pm\frac{2\gamma_\infty}{rRT\rho_\infty}, \qquad (32)$$

where p is the equilibrium vapor pressure over a spherical surface of a liquid of radius r, p_∞ is the value of p for a flat surface (at $r = \infty$), γ_∞ is the surface tension of a liquid for a flat surface, R is the gas constant, T is the temperature, and ρ_∞ is the molar density of the liquid in the bulk phase. The "plus" sign refers to a convex, and "minus" to a concave surface of the liquid. In the case of a drop, its vapor pressure increases with decreasing drop size (this case is illustrated by curve *2* in Fig. 3). The smaller the drop, the more noticeable the effect described by Eq. (32), and, therefore, it is often called the equation for the vapor pressure of small drops. In fact, the Kelvin equation is an asymptotic relation just for large drops in the sense that their radius must be much larger than the molecular sizes. The case of nanodroplets, and, moreover, limit $r \to 0$ cannot be discussed within the framework of the Kelvin equation.

Nevertheless, if the Kelvin equation is an asymptotic relation, then, in addition to the main asymptotic term represented by Eq. (32), there must also be a correction term (of the next order in terms of curvature). This correction was found and gave the Kelvin equation the form [59]

$$\ln\frac{p}{p_\infty} = \pm\frac{2\sigma_\infty}{rRT\rho_\infty}\left[1 \mp \left(\sigma_\infty\chi_\infty + \frac{2\Gamma_\infty}{\rho_\infty}\right)\frac{1}{r}\right], \qquad (33)$$

where χ is isothermal compressibility and Γ is adsorption.

Be that as it may, with or without correction, the Kelvin equation remains an asymptotic relation for large

r. The case of small particle sizes is not covered by it. Moreover, there is experimental evidence of nanoparticles behaving in direct opposition to the Kelvin equation. Such particles are, for example, surfactant micelles, for which it is precisely established that their size increases with the surfactant concentration in the solution, and, hence, with the chemical potential (not to mention the vapor pressure) [60–62]. Micelles do not have a macroscopic analog, and it is impossible to say how they behave in the range of the Kelvin equation. However, small particles often form equilibrium populations, and, as it turned out, it is the thermodynamics of aggregative equilibrium that can predict the behavior of the chemical potentials of small particles. The equilibrium population is characterized by the size distribution of molecular aggregates. Of particular importance are the extrema on the distribution curve: they correspond not only to aggregative (like all other points on the distribution curve), but also to phase equilibrium [63, 64].

In the theory of aggregative equilibrium, a remarkable relation was found [65]

$$\left(\frac{d\mu}{dn_e}\right)_{T,p} = -kT\left(\frac{d^2 \ln a_n}{dn^2}\right)_{n=n_e}, \tag{34}$$

where μ is the chemical potential of the substance in the aggregative system, n is the aggregation number, n_e is the aggregation number corresponding to the extremum on the distribution curve, and a_n is the activity of the molecular aggregate with the aggregation number n. The derivative on the left characterizes the dependence of the chemical potential on the extreme particle size. This is a real physical addiction. The right derivative refers to the curve of the equilibrium distribution of the activities of molecular aggregates according to their sizes. And this is already amazing: just looking at the distribution curve, using Eq. (34), we determine how the system will behave when the physical state changes! The maximum corresponds to stable particles, for example, surfactant micelles. For it, the second derivative appearing in Eq. (34) is negative, and then Eq. (34) predicts an increase in the chemical potential of a micelle with an increase in its size. This is directly opposite to the prediction of the Kelvin equation. In the case of a minimum on the distribution curve (corresponding to unstable phase or micellar nuclei), the prediction of Eq. (34) agrees with the prediction of the Kelvin equation. Thus, phase nuclei behave in the same way at large and small sizes (which depend on the degree of supersaturation of the parent phase): their chemical potential always increases with decreasing nucleus size.

Equation (34) is of fundamental importance for the thermodynamics of aggregative systems, and it can be safely attributed to the main laws of colloidal science. The establishment of such a law [65] should be considered a discovery.

3.4. Phase Rule

It seems that the phase rule is the most famous result of all the infinitely many things that Gibbs did. In its classic formulation, it reads

$$f = n - r + 2, \tag{35}$$

where *f* is the variance (number of degrees of freedom) of an equilibrium heterogeneous system, *n* is the number of independent components, and *r* is the number of macroscopic phases. The number 2 implies temperature and pressure (which, in the case of macroscopic phases, is the same throughout the system at equilibrium and provided that all interfaces can be considered flat). In each case, the phase rule determines not only the number of degrees of freedom, but also the maximum possible number of phases (for example, the number of phases cannot be more than three for $n = 1$, the well-known triple point). Note that Gibbs derived the phase rule from the Gibbs–Duhem equation

$$dp = s_v^\alpha dT + \sum_{i=1}^{n} c_i^\alpha d\mu_i, \tag{36}$$

where *p* is pressure, *s* is the entropy density, *T* is temperature, c_i and μ_i are the concentration and chemical potential of component *i*, respectively, α is the phase symbol. The number of variables in Eq. (36) is $n + 2$, and the number of Eqs. (36) coincides with the number of phases. Hence, Eq. (35) follows.

Equation (35) refers to a bulk multiphase system. But phase transitions can also occur on the surface (they are called two-dimensional). In addition, colloidal science is characterized by the presence of curved interfaces, and it is clear that the phase rule is inapplicable in the form of Eq. (35). Initially, its generalization went along the lines of taking into account the curvature of interfacial

surfaces and two-dimensional phase transitions [66]. For example, if all phases are separated by curved surfaces, then, in accordance with the Laplace equation, each of the phases has its own pressure, different from the others. Then the number of variables increases by $r − 1$, and we get $f = n + 1$. Typical for colloidal systems is the simultaneous presence of both macroscopic and dispersed three-dimensional and two-dimensional phases. For this general case, the author formulated the phase rule [67]

$$f = n − r_0 − p_0 + z + y + 1, \qquad (37)$$

where r_0 is the total number of bulk phases having at least one flat surface on their boundary; p_0 is the total number of surface phases having at least one straight line at their boundary; z is the number of bulk multiphase regions with the same pressure; y is the number of surface regions with the same surface tension.

We note the most important special cases of Eq. (37). For a system with only flat surfaces and rectilinear boundaries [66]

$$f = n − r + 2 − (p − l), \qquad (38)$$

where p is the number of two-dimensional phases, l is the number of interfacial surfaces. For a system with only curved surfaces and geodesic linear boundaries [66]

$$f = n + 1 − (p − l). \qquad (39)$$

Finally, in the absence of two-dimensional phase transformations, Eq. (36) is simplified to [68]

$$f = n − r_0 + z + 1. \qquad (40)$$

Everything said above about the phase rule applied to open systems. For closed and partially open systems, as well as systems in a rigid and/or adiabatic shell, both variance and total variance [69] are estimated, including phase masses as variables (which, under certain conditions, can play the role of state parameters). The calculation of both types of variance in capillary systems was carried out in detail in the monograph [60–62]. The pinnacle of all these generalizations is the variability of capillary systems in the presence of chemical reactions.

Here the number of components is replaced by the number of reactants, and matrices of stoichiometric reaction coefficients are used. The main result is written as [70]

$$f = c − k − r − p + x + y + z − b + s^*, \qquad (41)$$

where c is the total number of substances; b is the number of substances for which the system is closed; k is the rank of the matrix of stoichiometric coefficients of all substances; r and p are the number of bulk and surface phases, respectively; x, y, z are the total number of regions homogeneous in temperature, surface tension and pressure, respectively; s^* is the rank of the concentration-stoichiometric matrix of immobile substances (which do not leave the system).

3.5. Gibbs Adsorption Equation

The equation that Gibbs derived for the surface tension of liquids is now commonly known as the Gibbs adsorption equation. In its classical form, it is written as

$$d\sigma = −\bar{s}dT − \sum_i \Gamma_i d\mu_i, \qquad (42)$$

where $\bar{s}$ is the entropy excess per unit of dividing surface, and Γ_i is the absolute adsorption of component i (its excess per unit surface). Eq. (42) is an analog of the Gibbs–Duhem equation for the two-dimensional case, but if in the latter all quantities are uniquely determined physically, in the former all excesses depend on the position of the dividing surface. For a curved interface, the tension surface is chosen as the dividing surface, which makes Eq. (42) self-sufficient. In the case of a flat boundary, Gibbs considered Eq. (42) together with two Gibbs–Duhem equations for adjacent bulk phases, which led to a change in the coefficients at dT and $d\mu_i$ and a decrease in the number of chemical potentials by unity. The modified coefficients are invariant to the position of the separating surface, and Eq. (42) acquires a physical meaning. Formally, everything looks as if we chose a dividing surface from the condition that the absolute adsorption of one of the components (usually a solvent, such a surface is called equimolecular) is equal to zero. Then all other adsorptions become relative, which will be assumed below for all adsorptions in Eq. (42).

The development of the Gibbs adsorption equation took place in two directions: for an electrolyte solution and for a solid.

Electrolyte solution. Fixing the temperature and expressing the chemical potentials in terms of concentrations and activity coefficients , we obtain from Eq. (42) the equation of the surface tension isotherm

$$d\sigma / kT = -\sum_i \Gamma_i d \ln(c_i f_i), \qquad (43)$$

which is valid for a liquid mixture of particles of any nature, including ions. But for ions, the individual activity coefficients are difficult to determine, and therefore, in practice, the average activity coefficients of electrolytes are used. The corresponding transformation of Eq. (43) suggests itself, and one can only be surprised that it was not done before the author's work. However, the result looks somewhat cumbersome [71]:

$$d\sigma / kT = -\sum_r \Gamma_r d \ln(c_r f_r) - \sum_k \Gamma_k \nu_k d \ln(c_k f_{k\pm})$$
$$+ \sum_{k \neq s} \Gamma_k c_s d \ln(c_k / c_s) \sum_i \left(\nu_{ik} \nu_{is} / \sum_t c_t \nu_{it} \right). \qquad (44)$$

Here, the subscript r refers to the non-electrolytes present in the system, the subscripts k, s and t refer to the electrolytes (they run through the same values), and the subscript i refers to the ions; ν_{ik} is the stoichiometric coefficient of ion i in electrolyte k (the number of ions of type i formed during the dissociation of one molecule of electrolyte k) and $\nu_k \equiv \Sigma_i \nu_{ik}$ is the total number of ions formed during the dissociation of one molecule of electrolyte k. The first two terms on the right-hand side of Eq. (44) look rather trivial, but the third one (with triple summation) is of interest. Firstly, it does not contain activity coefficients, and, secondly, it is realized only if different ($k \neq s$) electrolytes have common ions (only then the product $\nu_{ik}\nu_{is}$ is nonzero).

We add that the third term in Eq. (44) is also insidious, since the possibility of its implementation is not immediately visible. Suppose we deliberately take two electrolytes that do not contain common ions, say, sodium alkyl sulfate $NaSO_4R$ (R is the symbol of the alkyl group) and $CaCl_2$ and dissolve in water. Both salts dissociate completely, and the four ions that they form in different combinations give four neutral substances related by the equation

$$2NaSO_4R + CaCl_2 = Ca(SO_4R)_2 + 2NaCl.$$
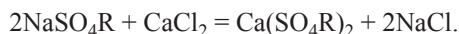
In the presence of such a coupling equation, only three of the four substances presented can be considered

independent components, but they contain common ions, so the third term in Eq. (44) cannot be discarded. Note that the written equation also reflects the real chemical process. When dissolved, the surface-active alkyl sulfate ion is adsorbed on the surface and attracts counterions, among which the calcium ion will predominate, since it is doubly charged and attracted more strongly.

Solid. Since Eq. (42) was derived by Gibbs only for a liquid surface, the generalization to the case of a solid body suggests itself. The dualism of surface tension discovered by Gibbs also requires the dualism of the adsorption equation, i.e. its representation in terms of both mechanical surface tension $\hat{\gamma}$) (generally written as a tensor) and thermodynamic surface tension σ. The task of finding them was completed by the author to the full, but since the expressions for γ are more cumbersome, we will restrict ourselves here to formulations in terms of σ, referring the interested reader to the review [42].

The first derivation of the Gibbs adsorption equation for the thermodynamic surface tension of an isotropic solid surface was given by Ericsson [52]:

$$d\sigma = -\overline{s}dT + (\gamma - \sigma)d \ln A - \sum_i \Gamma_i d\mu_i. \qquad (45)$$

For liquids, $\gamma = \sigma$ and Eq. (45) goes over to Eq. (42). The author generalized Eq. (45) to the case of an anisotropic solid surface [53]:

$$d\sigma = -\overline{s}dT + (\hat{\gamma} - \sigma\hat{1}) : d\hat{e}^\sigma - \sum_i \Gamma_i d\mu_i, \qquad (46)$$

where $\hat{e}^\sigma$ is the surface strain tensor and $\hat{1}$ is the unit tensor. Note that all chemical potentials in Eq. (46) refer to the fluid phases from which adsorption occurs. The chemical potential of a solid body (we denote it as $\hat{\mu}_j$, this is also a tensor) is not included in these equations, it is hidden in the difference of tension tensors, not to mention that the dividing surface for a solid body is chosen from the condition $\Gamma_j = 0$. It must be said that the tensorial nature of the chemical potential enters consciousness chemists with great difficulty (this is where the revolution in the minds really takes place!). The idea itself does not belong to the author (once it was put forward by the Ukrainian academician Y.S. Podstrigach), but the author accepted it and (in Russia in splendid isolation) actively promoted and substantiated [75] (in particular, the concept of the chemical affinity tensor was introduced, which is very important for the kinetics of solid-state reactions).

Finally, there is one more important circumstance in Eq. (46). The second term on the right-hand side disappears not only when passing to fluid phases (when $\hat{\gamma} = \gamma\hat{1}$ and $\gamma = \sigma$ but also in the case of an absolutely rigid body (then $d\hat{e}^\sigma = 0$). It turns out that in its classical form the Gibbs adsorption equation is applicable not only to liquids, but also to solid adsorbents whose deformation can be neglected (I imagine the jubilation of a large army of adsorption scientists who have been applying the Gibbs adsorption equation to solid adsorbents for decades, not knowing that it was derived only for liquids!). However, in reality, adsorption can be accompanied by deformation of a solid adsorbent (this phenomenon is called sorbostriction and is actively studied. The theory of sorbostriction was formulated in [76].

Let us now return to Eq. (46). It implies that the amount of adsorbent (the amount of immobile component j) is unchanged. If the adsorbent itself can dissolve or sublimate from different sides, then such a change in its shape (simulating deformation) should be excluded from the strain tensor, which leads Eq. (46) to an even greater generalization [74]

$$d\sigma = -\overline{s}dT + (\hat{\gamma} - \sigma\hat{1}):(d\hat{e}^\sigma - d\hat{N}_j/N_j) - \sum_i \Gamma_i d\mu_i, \quad (47)$$

where $\hat{N}_j$ is the mass displacement tensor showing the change in the amount of component j in different directions [43, 75]. This notation guarantees that the second term on the right-hand side of the adsorption equation (47) gives the work of surface strain.

3.6. Analogues of Konovalov's Laws for Interfacial Surfaces

Academician D.P. Konovalov was the successor to D.I. Mendeleev at the head of the Chair of General and Inorganic Chemistry at St. Petersburg University and the founder of the St. Petersburg thermodynamic school. Three laws for the equilibrium of a liquid solution with vapor brought him worldwide fame. We present them in Storonkin's formulation [69]: (1) the vapor pressure of the solution increases, and the boiling point decreases with an increase in the concentration of the component whose content in the vapor is greater than in the solution; (2) if the pressure and temperature of the coexistence of two binary phases have an extremum, then the phases have the same compositions; (3) under isothermal and isobaric

conditions, the compositions of the solution and vapor change symbatically. The first and third laws operate far from the critical point, and the introduction of the concept of an azeotrope (a mixture that cannot be separated by distillation) is associated with the second.

Since Konovalov's laws operate with the compositions of solution and vapor, the formulation of similar laws for surface phenomena requires the introduction of the concept of composition for the surface layer as well. It is absent in Gibbs thermodynamics, but it arises when constructing the thermodynamics of surface phenomena by the method of a layer of finite thickness, which was initiated by van der Waals. The very concept of the thickness of the surface layer is indefinite, and therefore it must be chosen large enough (with some margin from the adjacent phases) to ensure the existence of the surface layer as a physical body. This version of thermodynamics is inferior in severity to Gibbs thermodynamics, but quite strictly formulates regularities that are not related to a specific thickness value, and, most importantly, uses a powerful resource of thermodynamics of solutions. The development of this approach by the author [31, 68, 77] revealed one more advantage in comparison with the thermodynamics of surface phenomena based on the Gibbs method [78]: the possibility of using not only equalities as equilibrium conditions, but also inequalities expressing the conditions of stability (to them also belongs to the analogue of Konovalov's third law).

An analog of the Gibbs adsorption equation in terms of a surface layer of finite thickness has the form [68]

$$ad\sigma = -s_{\alpha\sigma}dT + v_{\alpha\sigma}dp - \sum_{i,k=1}^{n-1}(x_i^\sigma - x_i^\alpha)g_{ik}^\alpha dx_k^\alpha. \quad (48)$$

where a is the molar area of the surface layer; x_i is the mole fraction of component i (subscripts i and k run over the same values), g is the molar Gibbs energy, $g_{ik} \equiv (\partial^2 g/\partial x_i \partial x_k)_{T,p}$, and $s_{\alpha\sigma}$ and $v_{\alpha\sigma}$ are differential molar entropic and volumetric effects of adsorption, n is the number of components in the system, the superscript α refers to the bulk phase, and the superscript σ refers to the surface layer. It is essential that all independent variables on the right-hand side of Eq. (48) refer to the bulk phase and are always known from experiment.

For a binary system ($n = 2$) under isothermal-isobaric conditions, Eq. (48) is simplified to the form

$$ad\sigma = -(x_1^\sigma - x_1^\alpha)g_{11}^\alpha dx_1^\alpha, \quad (49)$$

from which the analogues of the first and second laws of Konovalov immediately follow. From the thermodynamics of solutions, it is known that $g^\alpha_{11} > 0$ according to the stability conditions. Then from Eq. (49), we immediately obtain the rule

$$d\sigma/dx^\alpha_1 < 0, \ \text{if} \ x^\sigma_1 > x^\alpha_1. \tag{50}$$

This is nothing but the well-known rule of surface activity in colloidal science. It also follows from the Gibbs adsorption equation, but now we see that this is an analogue of Konovalov's first law. From Eq. (49), the surface azeotropy rule also follows:

$$d\sigma/dx^\alpha_1 = 0, \ \text{if} \ x^\sigma_1 = x^\alpha_1, \tag{51}$$

which is an analogue of Konovalov's second law. Note that, typically, the temperature and pressure extrema do not coincide with the surface tension extremum, so that when the liquid and vapor compositions coincide, the composition of the surface layer, as a rule, is different. This creates the possibility of separating the components of the azeotrope by surface methods. In other terms, the rule expressed in Eq. (51) can also be derived from the Gibbs adsorption equation. As for the analogue of Konovalov's third law (far from the critical point)

$$dx^\sigma_1/dx^\alpha_1 > 0, \tag{52}$$

then, as noted above, it is a consequence of the stability conditions of a real surface layer [31], and therefore it is impossible to obtain it from Gibbs thermodynamics. As it turned out, condition (52) is practically useful for estimating the minimum possible thickness of the surface layer. The point is that when calculating the composition of the surface layer (from experimental data on surface tension or Gibbs adsorption), its thickness is postulated, and if it is taken too small, condition (52) is violated [77, 79]. In this way, for example, it was proved that the surface layer of the solution is typically not monomolecular (at least two monolayers are needed). This method gives a strong increase in the thickness of the surface layer of the solution near the separation point, and this prediction is in excellent agreement with the results of an ellipsometric study [48].

4. NANO-CORRECTIONS TO BASIC LAWS

Hurricanes are given names, and one, I remember, was called El Niño ("baby" in Spanish). In the nineties, we were hit by a hurricane that I would call El Nano (almost Nanos, "dwarf" in Greek), but it was a flurry of social science movement. It originated in Japan and was intended to study the particles of matter in the nanometer range, where they seem to have special properties. Kitsch was formed with the involvement of a mass of researchers who did not even suspect the existence of a colloidal science dealing with such problems for more than one century (the author even had to speak on this issue at a general meeting of the Russian Academy of Sciences). The creation of a dozen new international nano-journals speaks about the power of the movement. The term "nano-science" appeared, and in general many words beginning with the prefix nano-, and colloidal science, a kind of "porphyry-bearing widow", became barely audible. This is not surprising: only colloid scientists are engaged in colloidal science, while everyone has begun to engage in nanoscience. It was useless to argue and defend something here. But there was also a good way out for colloid science: to join the ranks of nanoscience and, using its advantage, take a leading position in it. And so it happened. We used to say "highly dispersed" or "ultradispersed," but now we say "nanodispersed" and calmly continue to work. We will start this section with the work of 1980, when nanoscience did not yet smell, and colloidal science was doing its job in the nanometer range as well [80].

4.1. The Gibbs–Curie Principle

In 1956, a postage stamp was issued in the USSR with a portrait of the "great French physicist" Pierre Curie (dedicated to the 50th anniversary of his ridiculous death in a Paris accident). It seems that this fact is enough to assess the scale of the personality of Marie Curie's husband. In this case, we are talking about his publication [81], where the condition for the surface free energy minimum for the equilibrium shape of a crystal was established. Seven years earlier, this condition had been obtained by Gibbs, but his work became known in Europe only half a century later. Slightly digressing, we note that such situations are typical for Gibbs. The most amazing of them happened with the participation of the author, who discovered in the works of Gibbs a completely rigorous, but purely verbal (!) proof of the abridged Le Chatelier-Brown principle (these authors published much

later). Me and M.M. Schultz translated Gibbs' proof into the language of formulas and published [82]. It can be said that Gibbs's priority was restored over the course of a century. But it is necessary to pay tribute to those who independently reproduced something from Gibbs, thereby, as it were, standing on the same level with him.

In the classical formulation, the Gibbs–Curie principle is written as

$$\sum_j \sigma_j \delta A_j = 0 \ (T, V, m = \text{constant}), \tag{53}$$

where σ is the thermodynamic surface tension (the work of forming a surface unit by breaking or cutting) of a single crystal face with area A, T is the temperature, V is the single crystal volume, m is its mass, and j is the face number. From Eq. (53), one can deduce Wulf's theorem (ordinal see [31, 32] for the correct derivation, even Yu.V. Wulf's own derivation was incorrect)

$$\frac{\sigma_j}{h_j} = \text{ constant.} \tag{54}$$

where h_j is the distance of face j to some fixed point inside the crystal (Wulf's point). The meaning of the condition expressed in Eq. (54) is that the higher the surface tension of the face, the farther it is from the Wulf's point and, therefore, the smaller its area. The pattern expressed by Eq. (54) was established by Yu.V. Wulf experimentally.

Equation (53) and (54) refer to macroscopic crystals. On going to nanocrystals, two types of corrections arise. The first is taking into account the thermodynamic linear tension κ of the edges of the crystal, which changes the Wolfe theorem to the form

$$\frac{\omega_j}{h_j} = \text{ constant}, \ \omega_j \equiv \sigma_j + \sum_k B_{jk} \kappa_k. \tag{55}$$

where κ_k is the linear tension of the edge k and B_{jk} are the coefficients depending on the orientation of the faces of the single crystal; the summation is performed over all edges adjacent to face j. The second kind of corrections is related to the fact that macroscopic bodies are at rest (and therefore their shape is visible), while nanoparticles participate in Brownian motion and, due to Brownian rotation, everything appears round. As you know, in order to see the shape of a body, you need to stop its rotation.

The free energy F of a nanoparticle can be written as

$$F = F^{00} - kT \ln Q_{\text{tr}} Q_{\text{rot}}. \tag{56}$$

where F^{00} is the free energy without taking into account the contributions of the translational and rotational motion of the particle as a whole, and Q_{tr} and Q_{rot} are the partition functions of these contributions given by the expressions

$$Q_{\text{tr}} = \Lambda^{-3} \equiv (2\pi mkT)^{3/2} h^{-3}, Q_{\text{rot}} = \Lambda_{\text{rot}}^{-3} \equiv (2\pi \bar{I}kT)^{3/2} h^{-3}. \tag{57}$$

where Λ is the de Broglie wavelength and Λ_{rot} is its rotational analogue, h is Planck's constant and $\bar{I} \equiv (I_1 I_2 I_3)^{1/3}$ is the average moment of inertia of the crystal ($\bar{I}_i$ is the three main moments of inertia).

It can be seen from Eq. (56) that only when the second term is neglected, the Gibbs equilibrium principle $\delta F = 0$ reduces to the Gibbs–Curie principle $\delta F^{00} = 0$. For nanoparticles, such neglect is incorrect. Taking into account that, according to Eq. (57), the partition function of the translational motion does not depend on the shape of the crystal, the generalized Gibbs–Curie principle can be written as [80]

$$\delta F^{00} + kT \delta \ln \Lambda_{\text{rot}}^3 = 0 \ (T, V, m = \text{constant}), \tag{58}$$

or

$$\sum_j \omega_j \delta A_j - \frac{3}{2} kT \delta \ln \bar{I} = 0 \ (T, V, m = \text{constant}). \tag{59}$$

Among the numerical estimates, there is an example when the nano-correction to the Gibbs–Curie principle reaches 8% [80].

In [80], a more general formulation of the generalized Gibbs–Curie principle was also proposed for nanoparticles that do not have a polyhedral shape

$$\oint_A \sigma \delta dA - \frac{3}{2} kT \delta \ln \bar{I} = 0 \ (T, V, m = \text{constant}), \tag{60}$$

where the integration is performed over the entire surface. In particular, this formulation was used in studying the shape of micelles [60–62].

4.2. Condition of Phase Equilibrium of a Soluble Nanoparticle

So far, we have used Gibbs' results, which are too well-known to refer to. But now the situation is changing. We turn to less known, but fundamentally important results of the classic of science, and it is necessary to decide what to refer to. In the United States, Gibbs' works

were reprinted twice, in 1906 and 1928, both editions being identical. They included two volumes, the first of which (Thermodynamics) will be the subject of our citation [83]. In the USSR, Gibbs was also published twice: the first time (the first volume) in 1950, edited by V.K. Semenchenko, and the second (both volumes) in 1982, edited by D.N. Zubarev [84]. The first translation was not entirely successful, besides spoiled by a number of erroneous editorial comments. The second one satisfies all the requirements, but, unfortunately, is not identical to the English edition (page numbers do not match), so when citing the text, we must separately indicate the pages in [83] and [84]. But it is most reliable to use the Gibbs numbers of the formulas that we will insert into our text (naturally, in our notation).

As is known, the equilibrium condition for fluid phases in chemical thermodynamics is the equality of chemical potentials of substances in both phases. In this case, each phase is considered homogeneous in terms of the chemical potentials of its components. But for solids, even this condition is not satisfied. Any solid body has a lattice (regular for crystals and disordered for amorphous bodies), the components of which (they are called immobile) are not able to move in space (we idealize a solid body, considering it defect-free). But the mechanism of equalizing the chemical potential just consists in the movement (diffusion) of the substance, and, thus, in a solid body, the implementation of such a mechanism is impossible. Gibbs noted that in the true equilibrium of a solid particle with its solution, the chemical potential of the substance of the particle cannot be the same in both phases [83, pp. 317–321; 84, pp. 313–317]. For an isotropic amorphous particle (phase α), he wrote down the condition of material equilibrium with his solution (phase β) in the following form [83, 84, Eq. (661)]:

$$\mu_j^\beta = \frac{f^\alpha + p^\beta + 2c\sigma}{c_j^\alpha}, \qquad (661)$$

where μ_j^β is the chemical potential of the solute, f^α and c_j^α is the density of free energy and matter in the solid, p^β is the pressure in the solution, c is the average curvature of the surface, and σ is the thermodynamic surface tension. A similar formula was also derived by Gibbs for a single crystal [83, 84, Eq. (665)]:

$$\mu_j^\beta = \frac{f^\alpha + p^\beta}{c_j^\alpha} + \frac{\sum_k l_k(\sigma_k \csc\varphi_k - \sigma \ctg\varphi_k)}{c_j^\alpha A}, \quad (665)$$

where σ and A are the thermodynamic surface tension and the area of the face in contact with the solution (for which the equilibrium condition is written), σ_k is the value of σ for the kth adjacent face that has the angle φ_k and length l_k of a common edge with the selected face.

Subsequently, both the equations (we wrote them down with Gibbs' numbers) were improved and extended to multicomponent systems and solid media [85, 86]. But the main limitation of Eqs. (661) and (665) (specially stated by Gibbs), that the state of the particle does not change during dissolution (this means that Gibbs considered a macroscopic particle), remained unshakable until the works of the author [87, 88]. They introduced a correction for a change in state. In essence, this is a nano-correction, which appears during the transition from macroscopic bodies to nanoparticles. After introducing the correction, Eq. (661) takes the form [87, 88]

$$\mu_j^\beta = \frac{1}{c_j^\alpha}\left[f^\alpha + p^\beta + 2c\sigma + \frac{d\sigma}{dN} \right], \qquad (61)$$

where N is the normal to the particle surface. For a spherical particle of radius R, Eq. (61) takes the form

$$\mu_j^\beta = \frac{1}{c_j^\alpha}\left[f^\alpha + p^\beta + \frac{2\sigma}{R} + \frac{d\sigma}{dR} \right]. \qquad (62)$$

Equation (665) is generalized similarly:

$$\mu_{j(nn)}^\beta = \frac{f^\alpha - E_{nn}^\beta}{c_j^\alpha} + \frac{\sum_k l_k(\sigma_k \csc\varphi_k - \sigma \ctg\varphi_k)}{c_j^\alpha A}$$
$$+ \frac{1}{c_j^\alpha}\left[\frac{d\sigma}{dN} + \frac{1}{A}\sum_k A_k \frac{d\sigma_k}{dN} \right], \qquad (63)$$

where E_{nn}^β is the normal component of the stress tensor. It is replaced by hydrostatic pressure ($E_{nn}^\beta = -p^\beta$) if the nanocrystal is in a liquid saturated solution (the case considered by Gibbs). Then we arrive at the relation

$$\mu_{j(nn)}^\beta = \frac{f^\alpha + p^\beta}{c_j^\alpha} + \frac{\sum_k l_k(\sigma_k \csc\varphi_k - \sigma \ctg\varphi_k)}{c_j^\alpha A}$$
$$+ \frac{1}{c_j^\alpha}\left[\frac{d\sigma}{dN} + \frac{1}{A}\sum_k A_k \frac{d\sigma_k}{dN} \right], \qquad (64)$$

which differs from the Gibbs Eq. (665) only by the correction terms related to the dependence of the surface tension on the nanocrystal size during its dissolution.

The introduction of nano-corrections makes the Gibbs formulas more universal, but all this left an alarming impression associated with Gibbs's statement about the inequality of the chemical potential of the substance of the particle in it and the surrounding solution at true equilibrium between the particle and the solution. How so? After all, the homogeneity of the chemical potential at equilibrium is the alpha and omega of chemical thermodynamics! In this regard, an additional study was undertaken [89], which turned out to be especially important for the interpretation of Gibbs' results. We have shown that if we compare the chemical potentials of the substance of a particle in bulk phases, i.e. inside the particle and the surrounding solution, then they are indeed different. It was already established in [73] that when moving along the normal from the surface into the depth of a solid, there is a chemical potential gradient (it is this gradient that is responsible for the dualism of surface tension). This means that the chemical potential on the surface of a solid is always different from its value inside the solid. At the same time, it was shown that the surface monolayer of a particle (only it is in contact and in true equilibrium with the solution) has a chemical potential value coinciding with the chemical potential of the substance j in solution [89]:

$$\mu_j^{\alpha(\sigma)} = \mu_j^{\beta}. \tag{65}$$

Thus, everything falls into place, and the material equilibrium is characterized by the equality of chemical potentials. In conclusion, we note an amazing thing: the process of comprehending Gibbs continues into the 21st century!

5. DISCOVERY OF NEW PHENOMENA

As you know, the discovery of new phenomena occurs in practice and requires experimentation. But, passing to this section, we do not say goodbye to thermodynamics. The latter either predicts a new phenomenon and "gives a tip" to the experimenter, or explains it after the discovery. A good illustration of this is the study of the dependence of surface tension on pressure.

5.1. Surface Tension Versus Pressure and Surface Properties of Water

This story begins with work [90], where the decrease in the surface tension of water and hexane at the interface

with different gases (He, H_2, N_2, etc.) was studied with increasing pressure. Helium has been succinctly said to have "no effect." The rest of the gases unanimously lowered the surface tension. Immediately, such a character of the dependence of surface tension on pressure was confirmed by a theory (alas, not flawless). However, the thermodynamic analysis carried out in monographs [31, 32, 68] showed that the drop in surface tension is associated with the solubility of gases. If the gas is insoluble in the liquid, then with increasing pressure the surface tension of the liquid should increase, although this may be weakly expressed. If we take a closer look at the plots of [90], then this is exactly what happens: for the least soluble helium, there is an effect, but it is opposite in sign.

Thermodynamic analysis also showed that this rare case opens up new possibilities for surface studies. If the gas only presses, but does not dissolve itself (the criterion for this is an increase in surface tension), then by measuring the dependence of surface tension on pressure, one can calculate the self-adsorption of a pure liquid, i.e. determine its surface density. To carry out similar studies of a number of liquids at the boundary with helium, a high-pressure unit was assembled at the Laboratory of Surface Phenomena of the Leningrad State University. In the experiments, the temperature was also varied, which made it possible to determine the change not only in the density, but also in the entropy in the surface layer. The results obtained [91–93] demonstrate the special behavior of water. Based on the surface monolayer, the decrease in density in non-polar liquids (CCl_4, C_6H_6) was about 3%, for polar liquids (C_6H_5Cl, C_6H_5Br, $C_6H_5NO_2$) it was slightly more (up to 6%), and for water it was as much as 15%. But even more attention is drawn to the temperature dependence of the surface density. If for other liquids the density of the surface layer typically decreases with increasing temperature, then for water it passes through a maximum, but not at 4°C, as for bulk water, but somewhere around 50°C when calculating both mono- and bimolecular surface layer. Water has repeatedly surprised researchers with its properties. Now we see: also with surface properties.

5.2. Wetting Anisotropy

This interesting phenomenon was first reported in [94]. If we take a rectangular rubber plate with polished surfaces (to avoid the effect of roughness), stretch it in one direction along the surfaces and place a liquid drop

with a finite contact angle on it, then the drop will take an oval shape in plan, and the contact angle in the direction of stretching will be smaller, than across the direction. This is the wetting anisotropy. The authors' explanation was very simple: by stretching the plate, we increase the surface tension in the direction of stretching. Then, according to the Young equation (26), the contact angle must be smaller in the direction of tension. Everything would be fine, but, unlike the mechanical surface tension γ (in the general case, the tensor $\hat{\gamma}$), which is included in the Laplace equation, the thermodynamic surface tension σ in the Young equation is work, i.e. a typical scalar that cannot be related to any directions. For someone familiar with surface tension dualism, one look at Eq. (26) is enough to understand that it forbids any anisotropy.

Shortly after this publication, one of the authors, L.A. Akopyan spoke at the permanent All-Union Seminar on the theory of surface phenomena in Leningrad, which I then led. He himself worked in the Leningrad branch of the Research Institute of the Rubber Industry (once his boss, the venerable Moscow scientist G.M. Bartenev, a specialist in physics and mechanics of polymers, also worked in the same research institute), so it is clear why the experiments were carried out on rubber. The report aroused great interest, and, most importantly, charged the audience (and not least myself) with a puzzle that took years to solve. The classical theory of wetting, including the Young equation, assumed that the solid body was indeformable, and rubber and elastomers generally belong to a different category. Obviously, this was the whole point! But the theory of wetting of deformable bodies did not exist then, and, in fact, it was necessary to create it.

In the Young equation, only one quantity $\sigma_{LV} = \gamma_{LV}$ refers to the fluid phases and, therefore, has the properties of mechanical surface tension. In particular, this is the force acting per unit length of the three-phase contact line of a drop on the surface of a solid body. Since this force is tension (opposite to pressure in sign), it will lift the surface, forming a bead along the three-phase contact line. Another force from the side of the drop is the Laplace capillary pressure, which is distributed uniformly over the entire surface SL and forms a deepening under the drop (Fig. 6). Obviously, the creation of a theory of wetting of deformable bodies (of course, elastic, since we are talking about an equilibrium theory), it was necessary to begin with the calculation of deformation within the framework of continuum mechanics and elasticity theory. The pioneer in the formulation of such a problem was Lester [95]. He
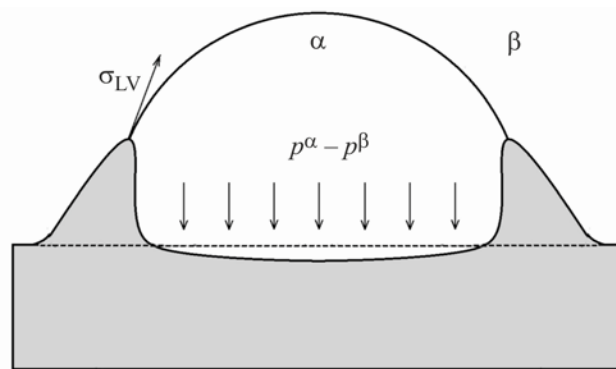

Fig. 6. Deformation of a solid water substrate by the influence of a drop. Dotted line showing surface before deformation.

proposed to set the surface tension in the form of a certain stress uniformly spread over the thickness of the surface layer. Such reasonable modeling was also adopted in our calculations [53–56]. The entire profile of the deformed plane was found, and the height of the bead was estimated at about $7\gamma_{LV}/E$. Having barely published this material, I was confronted by Ya.O. Bikerman [96]: say, such estimates have already been made a long time ago. I had to fight back and prove that all other formulas, including the Lester formula, are not suitable for estimating the height of the roller [57].

The performed calculations also included an estimate of the work of deformation, but how can it be used in the theory of wetting? Finally, a saving idea came up [48]: since this work is connected with the formation of a bead along the three-phase contact line, include it entirely in the linear tension. This makes it orders of magnitude larger than usual and makes it possible to noticeably influence the contact angle, if we keep in mind the generalized Young equation (27). But what does anisotropy have to do with it, because work remains work (i.e., a scalar quantity), no matter where you insert it? The moment of truth is coming, and I ask you, the reader, to be especially attentive. Uniaxial stretching of the elastomer leads to the orientation of polymer chains in the direction of stretching. If we now place a drop on the elastomer surface, then different sections of the three-phase contact line (along which the surface tension of the drop causes additional deformation of the substrate) will be differently oriented with respect to the elongated polymer chains. In the area where the three-phase contact line is perpendicular to them, the deformation (and, consequently, the work of deformation) will be minimal, since it is associated with

the bending of polymer chains (Young's modulus is maximum in this place). In the area where the line of the three-phase contact is parallel to the polymer chains, the deformation of the substrate is reduced to the movement of the chains as a whole (without bending them) and is much easier, and therefore the deformation itself and its work will be maximum (Young's modulus in this area is minimal). Now, regarding the effective linear tension of the three-phase contact line, we can say that it will be minimum across and maximum along the direction of sample stretching. Then the generalized Young equation (27) immediately leads to the conclusion that the contact angle of the drop should be minimal in the direction of tension and maximal in the transverse direction. This is exactly what is observed in the experiment and is called wetting anisotropy.

It turns out that the solution to the puzzle that L.A. Akopyan at the seminar, it took 6 years. But for a full-fledged discovery, this is not enough. We still need to prove that this solution is unique. Here is an example: when a rubber plate is stretched, microscopic wrinkles can form in the same direction, which, when wetted, play the role of grooves. But it is known that wetting is always better along than across the grooves. Here is an explanation of wetting anisotropy. Additional studies were needed, which were successfully carried out on the basis of the Leningrad Branch of the Research Institute of the Rubber Industry [97, 98]. The last point in this story can be considered [50] devoted to the influence of the roughness of the three-phase contact line on the contact angle under deformation. Unlike surface roughness, line roughness can be caused by surface tiling even if the surface is polished like a rubber sheet. Surface deformation changes the mosaic pattern and creates its own anisotropy. Accounting for this factor improves the agreement between theory and experiment in [97–99]. Thus, all questions were removed, and it was confirmed that the above explanation of wetting anisotropy is the only correct one.

6. MECHANOCHEMISTRY: NEW LAWS AND PHENOMENA

It is known that the mechanical state affects the rate of chemical reactions, and the latter, in turn, can lead to a change in the mechanical state. This is especially true for solid-state chemical reactions. Similar phenomena are studied by mechanochemistry, the very name of which suggests that we are talking about the combination of mechanics and chemistry. But what connects them and how? There is a third force, which is not talked about, but which, like the "grey eminence," plays a major role here, chemical thermodynamics. It is this theory that has made it possible to connect the chemical potential tensor and the stress tensor and create modern tensor mechanochemistry [75, 100–102], which we will rely on in this section.

6.1. Chemical Potential Tensor

It may be surprising that Gibbs, being not only the creator of chemical thermodynamics, but also an innovator in vector and tensor calculus, did not introduce the concept of the chemical potential tensor. However, there are objective reasons for this: the chemical potentials of immobile components in solid phases no longer play the role that the chemical potentials of mobile components play in fluid media. Be that as it may, Gibbs, in fact, substantiated the tensor nature of the chemical potential when he derived the equilibrium condition for a soluble crystal simultaneously with three liquid solutions at three different pressures in the main directions [83, 84, Eqs. (393)–(395)]:

$$F + p'V = \mu_j' N_j, \tag{393}$$

$$F + p''V = \mu_j'' N_j, \tag{394}$$

$$F + p'''V = \mu_j''' N_j, \tag{395}$$

where F, V and N_j are the free energy, the volume and number of crystal molecules, p is the pressure, μ_j is the chemical potential of the immobile (lattice forming) component of the crystal, the strokes mark three solutions that are in contact with the crystal in three main directions.

Let us now use the conditions of mechanical equilibrium

$$E_k = -p^{(k)}, \tag{66}$$

where k is the number of the main direction of the stress tensor $\hat{E}$ (or the number of strokes). Recall that the stress tensor is symmetrical and can always be reduced to a diagonal form

$$\hat{E} = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}, \tag{67}$$

where E_k ($k = 1, 2, 3$) are the principal values of the tensor (all normal, shear stresses are absent in Eq. (67)). It is this situation that is currently being considered. We substitute Eq. (66) into Eqs. (393)–(395) and write these three equalities compactly as

$$\frac{f^\alpha - E_k^\alpha}{c_j^\alpha} = \mu_{j(k)}^\beta \ (k = 1, 2, 3), \tag{68}$$

where $f \equiv F/V$ is the free energy density and $c_j \equiv N_j/V$ is the concentration of component j. Here we also introduced phase designations: α is the solid phase, β is the liquid solution. Now on the left side of Eq. (68) there are only quantities related to the crystal, and on the right to its solutions. Since there are three different chemical potentials on the right side if we introduce the chemical potential of a solid, then this can only be a tensor chemical potential. And it must be introduced in an independent way, and not from the equilibrium condition, because the chemical potential must exist under any conditions. Let us explain how this is done [75, 100].

Take the standard definition of chemical potential in thermodynamics

$$\mu_j \equiv \left(\frac{dF}{dN_j} \right)_{T,V,N_{i \neq j}}. \tag{69}$$

If the chemical potential is a tensor, then its thermodynamic conjugate quantity, the mass or the number of moles, must also be a tensor, which seems impossible in this case (mass is a typical scalar). However, in Eq. (69) the chemical potential is combined not with N_j but with dN_j and this changes the matter. A crystal can grow differently in different directions, and to characterize the entire process as a whole, we can introduce the mass displacement tensor

$$\hat{N}_j \equiv \begin{pmatrix} N_{j(11)} & N_{j(12)} & N_{j(13)} \\ N_{j(21)} & N_{j(22)} & N_{j(23)} \\ N_{j(31)} & N_{j(32)} & N_{j(33)} \end{pmatrix}. \tag{70}$$

Then the analog of Eq. (69) for the chemical potential tensor can be written in the form

$$\mu_{j(st)} \equiv \left(\frac{\partial F}{\partial N_{j(st)}} \right)_{T,\hat{V},N_{i \neq j}} (s, t = 1, 2, 3), \tag{71}$$

where $\hat{V}$ is the volume displacement tensor, which is introduced in the same way as the mass displacement tensor, but refers to the change in volume. The constancy of this value in Eq. (71) means that after adding a substance to a crystal at one of its boundaries, it must be returned to its previous position, i.e. perform a certain work of deformation, which is the measure of the component of the chemical potential tensor. The work will be different for different directions, and if the crystal grows not along the normal to the surface, but at a certain angle to it, then the shear deformation will also increase. The contribution of the immobile component j to the free energy is given by

$$(dF)_{\hat{V},N_{i \neq j}} = \hat{\mu}_j : d\hat{N}_j \equiv \sum_{s,t=1}^{3} \mu_{j(st)} dN_{j(st)}, \tag{72}$$

where the colon means the biscalar product of tensors.

From many provisions related to the introduction of the chemical potential tensor (see, for example, Eq. (68)), a fundamental regularity follows: *the anisotropy of the stress tensor in a solid entails the anisotropy of the chemical potential, giving the latter a tensor character*.

6.2. Chemical Affinity Tensor

In Gibbs' thermodynamics, not only phase, but also chemical equilibria are considered. The equilibrium condition for a chemical reaction is formulated as follows. Let there be a chemical reaction

$$\sum_i \nu_i' B_i' = \sum_i \nu_i'' B_i'', \tag{73}$$

where B_i and ν_i are the symbol of the i-th chemical substance and its stoichiometric coefficient; a stroke marks the substances that enter into a reaction, and two strokes mark the products of the reaction (they may also differ from the starting substances by their numbers). According to Gibbs, the equilibrium condition for reaction represented by Eq. (73) is written as

$$\sum_i \nu_i' \mu_i' = \sum_i \nu_i'' \mu_i'', \tag{74}$$

i.e. it is just that, in the same equation, the symbols of substances are replaced by their chemical potentials.

De Donder moved all the terms of Eq. (74) to the left side and called the resulting combination of chemical potentials the affinity of the chemical reaction A [78, 103]:

$$A \equiv \sum_i (\nu'_i \mu'_i - \nu''_i \mu''_i). \qquad (75)$$

The sign of affinity determines the direction of a chemical reaction. For $A > 0$, there is a direct reaction (from left to right), and for $A < 0$, the reverse reaction (73). The absolute value of the affinity determines the rate of the process. At $A = 0$, there is an equilibrium of the chemical reaction in accordance with Eq. (74). Thus, the greater the absolute value of A, the higher the rate of the process.

As applied to solid-state reactions (they are important for mechanochemistry), chemical potentials should be written in a tensorial form, but then the affinity becomes a tensor quantity. This is how the concept of the chemical affinity tensor arises [43, 75, 100]:

$$\hat{A} \equiv \sum_i (\nu_i \hat{\mu}'_i - \nu_i \hat{\mu}''_i). \qquad (76)$$

If mobile components (with a spherical chemical potential tensor) also participate in the reaction, then the notation for the latter is simplified. Separating the immobile (symbol j) and mobile (symbol i) components, we can write Eq. (76) as

$$\hat{A} \equiv \sum_j (\nu_j \hat{\mu}'_j - \nu_j \hat{\mu}''_j) + \hat{1} \sum_i (\nu_i \mu'_i - \nu_i \mu''_i), \qquad (77)$$

where $\hat{1}$ is the unit tensor, or, in terms of the components of the chemical affinity tensor,

$$A_{st} \equiv \sum_j (\nu_j \mu'_{j(st)} - \nu_j \mu''_{j(st)}) + \delta_{st} \sum_i (\nu_i \mu'_i - \nu_i \mu''_i), \quad (78)$$

where δ_{st} is Kroneker's symbol.

The main task of mechanochemistry is to establish a connection between the chemical affinity tensor and the stress tensor, which is solved by the methods of thermodynamics. In essence, this problem is a derivative with respect to establishing a connection between the chemical potential tensor and the stress tensor, because chemical affinity is always just some combination of chemical potentials. In many cases, a solid body participates in chemical reactions with its surface, and therefore the thermodynamics of surfaces is also important here. There is no doubt that the new quantity "chemical affinity tensor" will occupy an important position in the kinetics of solid-state reactions.

6.3. Mechanochemical Effect of Dissolution

My friend Academician M.M. Schultz was an excellent physical chemist. Once I asked him: "If you bend a KCl crystal plate and lower it into water, which side will dissolve faster: convex or concave?" He immediately perked up: "Just don't tell me the answer. I'll figure it out myself." Such a reaction usually indicates the simplicity of the question, but here it consists only in understanding it. The chain of possible response reasoning is easy to reconstruct. When the plate is bent, its convex part is stretched, and the concave part is compressed. These types of deformation differ in sign. Obviously, the side where the chemical potential is higher will dissolve faster. The work of deformation contributes to the chemical potential, but according to Hooke's law (not everyone knows mechanics, but everyone knows Hooke's law), the work is quadratic in deformation and, therefore, cannot depend on its sign. In turn, this means that both sides of the plate will dissolve at the same rate.

The answer is logical but wrong. Experiment shows that the concave side dissolves faster, and this already smells like a discovery, because you have to change your ideas. The first observations of this kind were made in the early 1980s at Odessa University by A.M. Dyachenko and his graduate student G.V. Berenstein, but paradoxical results hung in the air. At one of the conferences A.M. Dyachenko invited me to come to Odessa to sort things out on the spot. Upon closer acquaintance, it turned out that we have other points of contact. Surprisingly, our collaboration began with work on wetting on deformable surfaces [104, 105] (these references complement the literature on the discovery of wetting anisotropy). But work on the dissolution of the curved KCl plate continued. In particular, it was found that not only the dissolution rate, but also the equilibrium solubility for the two sides of the plate has different values. Obviously, there was some unaccounted factor in this case, and it soon became clear that it was nothing more than surface tension.

Clarifications are needed here. First, bearing in mind the dualism of the surface tension of a solid body, it should be noted that we are talking about mechanical (force) surface tension. Secondly, since not the entire surface layer, but only its monolayer, is in equilibrium with the solution, strictly speaking, we mean not the entire surface tension (which is an excess value), but only the stress related to the surface monolayer of the solid. In fact, here we abandon the Gibbs excess method and proceed to consider the real values of the monolayer (although the

difference here is small: it is known that the contribution of the monolayer to the surface tension can reach 90%). And you also need to take into account that for a solid body, the mechanical surface tension γ can have any sign. Thermodynamic surface tension σ is always positive in terms of stability (proved by Gibbs). Since for a liquid γ = σ, then for a liquid also γ is always positive.

Accounting for surface tension changes the whole picture of the prevailing ideas. First of all, it concerns mechanics, more precisely the classical theory of elasticity. Its Achilles' heel is the postulate of the absence of stresses in a body that is not subject to any external influences. In reality, a body of limited dimensions can, by its own molecular forces, create internal stresses at the surface. This is how surface stress ς occurs. If we turn now to a curved plate, then on one side the surface stress will add up with the resulting bending stress, and on the other, where the stress is opposite in sign, it will be subtracted from the surface stress. This breaks the symmetry (dictated by Hooke's law) and reveals the mechanochemical effect of the deformation sign. The total stresses, strains and changes in chemical potentials will be different on different sides of the plate, and therefore the rate of their dissolution will be different. Specifically, it will be possible to say which side will dissolve faster after the sign of the mechanical surface tension of the plate material is established (usually this sign is unknown).

Let us briefly formulate the theory of the phenomenon. Once the thermodynamic foundations of mechanochemistry have been built [75, 100, 101], it is much easier to do so than in our original publication [106]. We will proceed from the general relation connecting the chemical potential tensor of an ideally elastic solid body (component j, for simplicity, we assume that the body does not contain mobile components) with the stress and strain tensors at a given temperature

$$d\mu_{j(rr)} = v_j[\sum_{l,m=1}^{3}(E_{lm}-\delta_{lm}E_{rr})de_{lm}-dE_{rr}], (r=1,2,3), \quad (79)$$

where the diagonal component of the chemical potential tensor of the immobile component in the direction r $\mu_{j(rr)}$ is given as a function of the components of the stress E_{lm} and strain e_{lm} tensors (v_j is the molecular volume). Eq. (79) refers to the bulk phase and indicates that the chemical potential in the chosen direction depends on stresses not only in this direction, but in all other directions. Since dissolution occurs from the surface and is determined by

the state of the surface monolayer of the solid, there is no point in going over to surface excesses (this operation levels out the monolayer and is therefore undesirable). You just need to apply Eq. (79) to the monolayer, and as the direction r choose the normal to the surface ($r = 3$, 1 and 2 are directions along the surface). Then E_{33} is the normal stress in the environment (for example, atmospheric pressure with a minus sign), and is the only practically important component of the chemical potential, which we are the only ones dealing with (we can forget about the tensorial nature of the chemical potential and perceive it as a scalar). As for the surface tension, instead of it, in the surface monolayer there is a real tangential stress ς that is excessive with respect to the external medium (for simplicity, we consider the two-dimensionally isotropic case). If external stresses are applied to the surface of the body, they add up to and affect the dissolution, which is the mechanochemical effect.

Consider the dissolution of a bent (in direction 1) elastic isotropic plate. Integration Eq. (79) at a constant external pressure gives the following expression for the chemical potential of a convex surface [100]

$$\mu_{j(33)} = \mu_{j(33)0} + v_j(1-\kappa)\varsigma e_{11} + v_j\lambda e_{11}^2, \quad (80)$$

where κ and λ are elastic constants, and subscript 0 refers to the undeformed state. In the same notation for a concave surface

$$\mu_{j(33)} = \mu_{j(33)0} - v_j(1-\kappa)\varsigma e_{11} + v_j\lambda e_{11}^2. \quad (81)$$

Comparison of Eqs. (80) and (81) shows that the chemical potential of the plate substance, and, hence, the dissolution rate and solubility, will be different for the convex and concave sides, and this difference is due solely to the presence of surface stress ς.

Subtracting Eq. (81) from Eq. (80), we find

$$\Delta\mu_{j(33)} = 2v_j(1-\kappa)\varsigma e_{11}, \quad (82)$$

where Δ means the difference for the convex and concave sides. It can be seen from Eq. (82) that the predominance of one of the sides depends on the sign of the surface stress: the dissolution rate and solubility will be higher on the convex side if $\varsigma > 0$, and on the concave side, if $\varsigma < 0$. In cases where double electric layer (for example, when an ionic crystal contacts water), one can expect a negative surface charge since the surface monolayer of

a solid will play the role of one of the plates in which like-charged particles mutually repel each other. Such a result was obtained for single-crystal KCl plates [106]. A similar study was carried out on the dissolution of glass and silicon in HF and KOH solutions, respectively [107]. Note that Eq. (82) not only predicts the sign, but also allows one to directly estimate the value of ς since the left side of Eq. (82) is easily determined from solubility experiments. Calculation schemes have also been developed using kinetic experiments (then ς is found from the difference in the dissolution rates of opposite sides of a curved plate) [108]. This method, for example, was used to find the value of $\varsigma = 4.7 \times 10^8$ Pa in the study of the dissolution of a curved glass plate in an 18% HF solution [109].

6.4. Effect of Strain Sign in Stress Corrosion Phenomena

This discovery [110, 111] is related to the one described above and was undertaken under its influence. As an example, one could study any solid-state surface chemical reaction, but we chose the corrosion of metals for two reasons. First, this is a huge applied value of corrosion and, in particular, corrosion under stress, associated with direct financial costs in various areas of human activity. Second, considerable scientific material has already been collected on stress corrosion (see, for example, [112]) and certain regularities have been established. In particular, it is determined that any deformation of the metal increases the corrosion rate. From a thermodynamic point of view, this is obvious. Gibbs also showed that under conditions of constant pressure, the chemical potential of a solid is given by the density of free energy, and any deformation increases it.

In general, corrosion can be understood as the gradual destruction of a material during chemical reactions that occur when the material comes into contact with the environment. A typical example is the anodic dissolution of iron (Fe = Fe^{2+} + 2e) accompanied by the reduction of hydrogen (2H$^+$ + 2e = H$_2$). For such a process, the chemical affinity (more precisely, its normal component with subscript 33) has the form

$$A_{33} = \mu_{Fe(33)} - \mu_{Fe^{2+}} - 2\mu_e, \qquad (83)$$

where $\mu_{Fe(33)}$ is the chemical potential (more precisely, its normal component) of iron in the solid state on the surface of the sample, $\mu_{Fe^{2+}}$ is the chemical potential of

the iron ion in solution, and μ_e is the chemical potential of the electron. The value $\mu_{Fe^{2+}}$ is determined by the composition of the solution and does not depend on the mechanical state of the solid sample. The chemical potential of an electron μ_e, although it refers to a solid body, can be controlled regardless of the state of the lattice (for example, by setting the electric potential), since metal electrons are a mobile component of a solid body. Thus, only the chemical potential $\mu_{Fe(33)}$ on the right-hand side of Eq. (83) is directly affected by the deformation of the sample. The higher the chemical potential of iron in the solid state, the greater the chemical affinity, and, hence, the rate of transition of iron into solution. But the chemical potential, as already mentioned, at a constant external pressure is determined by the free energy density. Hence it follows that the deformation of the material always leads to the acceleration of its corrosion.

For a curved elastic plate in a corrosive medium, similarly to Eqs. (80) and (81), we obtain

$$A_{33} = A_{330} \pm v_j(1-\kappa)\varsigma e_{11} + v_j\lambda e_{11}^2, \qquad (84)$$

where in the double sign, plus corresponds to a convex, and minus to a concave surface; all other designations are the same as in Eq. (80). Eq. (84) leads to the conclusion that, due to the existence of surface stress ς, the corrosion rate is different on the convex and concave sides of the plate. At $\varsigma > 0$, the convex side of the plate should corrode faster, and at $\varsigma < 0$, the concave side of the plate. Thus, Eq. (84) predicts the effect of the sign of deformation on the corrosion rate of the material. Experimentally, this discovery was made [110, 111] within the walls of the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences. Let us briefly explain the essence of the experiment.

For experiments, plates of unalloyed steel 0.1–1 mm thick were taken and, after a fixed bend, were placed in a 35% HCl aqueous solution. The sample was periodically weighed to control its weight. One of the sides of the plate was covered with a protective varnish, so that the experiments with the concave and convex sides were carried out separately. The result of observations at short times is shown in Fig. 7, which shows that corrosion occurs faster on the concave side. However, the situation changes with time: the effect of the deformation sign is reversed, and the convex side becomes more active (Fig. 8). The explanation here is trivial: the destruction of the material in the process of corrosion begins with
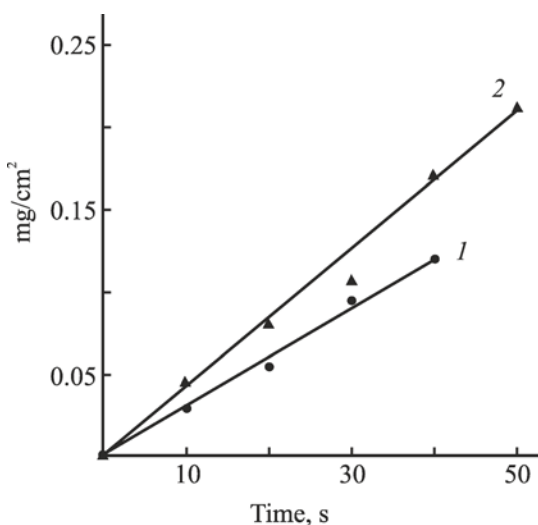
Fig. 7. Time dependence of the decrease in sample mass per unit area for the concave (*1*) and convex (*2*) sides of a curved steel plate in a 35% HCl solution. The slope of the lines gives the corrosion rate [110].
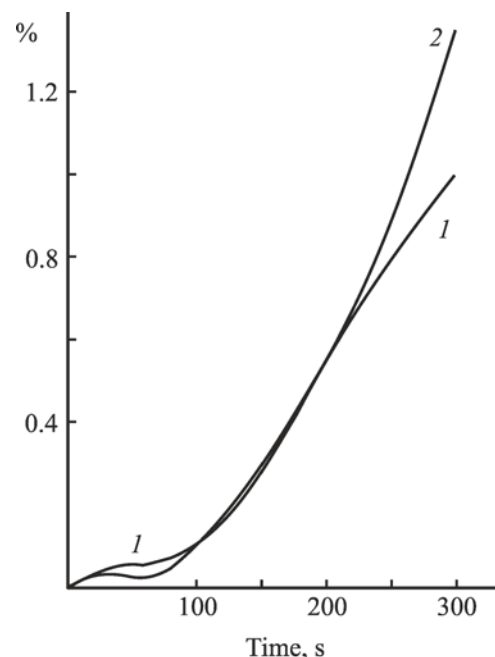

Fig. 8. Reversal of the warp sign effect. Curves of the decrease in the mass of the sample per unit area versus time for the concave (*1*) and convex (*2*) sides of a curved steel plate in a 35% HCl solution [110].

corrosion cracking. It begins, naturally, on the convex side and leads to an increase in the real surface and the flow coming from it. The only conclusion that can be drawn from this is that the study of the mechanochemical effect should be carried out at short times, when the destruction of the material has not yet begun.

After the first publications [110, 111], detailed studies of the mechanochemical effect of the sign of deformation in stress corrosion phenomena were carried out [113–115]. Experimental work was carried out both by the above-described gravimetric method and by the hydrogen method, in which the decrease in the mass of the metal during corrosion was determined by the volume of released hydrogen. In [115], this method was used not only to establish the mechanochemical effect itself, but also to estimate the surface stress $\varsigma = 5 \times 10^4$ MPa for complexly alloyed austenitic steel based on the results of experiments with a bent plate in a 3 M HCl solution.

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6.5. Mechanochemical Effects in Redox Reactions with Iron

The presence of the mechanochemical effect of the sign of deformation was also verified in a number of redox reactions involving iron [116]. The peculiarity of this study was that the mass of the plate did not decrease, but, on the contrary, increased due to the deposition of heavier metals (copper, silver, lead), and the experiments were carried out on a modernized setup that made it possible to carry out three measurements of the mass of the plate or solution per second with automatic registration on a computer [113, 117]. It should also be noted that different grades of steel were used, including steel with a reduced carbon content. The latter is of particular interest for two reasons. First, by using steel instead of iron to meet the
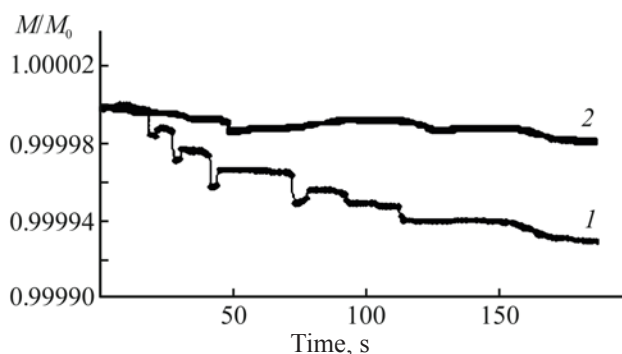
Fig. 9. Dependence of the relative mass M/M_0 of a 10% $AgNO_3$ solution on time during silver deposition on (*1*) concave and (*2*) convex sides of bent mild steel plates [116].

requirements of mechanics in terms of elasticity, we act to the detriment of the chemical requirements for the purity of the reagent. For chemistry, the less impurities in iron, the better. Second, steel with a minimum carbon content already shows signs of plasticity, and this reduces the cracking of the plate on the convex side, which interferes with the detection of the mechanochemical effect.

The purpose of the work was to study the effect of the sign of deformation in redox reactions occurring on the surface of steel plates in their contact with aqueous solutions of salts of other metals. Consider, as an example of a redox reaction, the interaction of iron and silver nitrate. When iron comes into contact with a solution of $AgNO_3$, a reaction occurs

$$Fe + 2Ag^+ = Fe^{2+} + 2Ag. \tag{85}$$
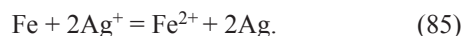
Here, the reducing agent, iron, donates electrons, and Fe^{2+} ions, being hydrated, go into solution. The oxidizing agent, a silver ion, accepts an electron, recovering to zero valence:

$$Ag^+ + e \rightarrow Ag \text{ (precipitate).} \tag{86}$$

Both elementary reactions take place at the point of contact of the iron with the solution, so that the electrons directly pass from the iron to the silver ions.

As for any other chemical reaction, the rate of a redox process is determined by its chemical affinity, which is a combination of chemical (electrochemical) potentials corresponding to the reaction stoichiometry. For the redox reaction in Eq. (85), the chemical affinity is given by

$$A = \mu_{Fe} + 2\mu_{Ag^+} - \mu_{Fe^{2+}} - 2\mu_{Ag}. \tag{87}$$

Let us see how the stress in steel plates affects the chemical affinity in Eq. (87). Obviously, an artificially created voltage can affect only the solid part of the system and does not affect the ions in solution. There are two such terms on the right-hand side of Eq. (87): μ_{Fe} and $-2\mu_{Ag}$, but at the initial stage of the process, the influence of the second is negligible. When a metal contacts water, a double electric layer is formed: iron ions partially go into solution, and the excess electrons remaining near the surface from the side of the solid phase create (due to their mutual repulsion) a negative voltage (positive two-dimensional pressure) in the surface monolayer and a negative contribution to the surface tension solid body. This leads to an increase in the chemical potential and chemical affinity in Eq. (87). When the plate is bent on the compressed (concave) side, the negative surface stress increases, and the chemical affinity in Eq. (87) increases even more. For the stretched (convex) side, the situation is reversed, which means that the rate of transition of iron into solution should be higher on the concave side of the plate than on the convex one.

The result of the experiment with silver, shown in Fig. 9 fully confirms this prediction. In the experiment, the change in the relative mass of the solution M/M_0 (M_0 is the initial value of the mass of the solution M), which decreases during the experiment, was determined. The study was carried out with steel plates with a reduced carbon content, which helped to avoid cracking of the convex side of the plate and to reveal the pure mechanochemical effect.

6.6. Mechanochemical Effect of the Sign of Strain in Wetting Phenomena

All the discoveries described above related to the effect of the sign of deformation were explained due to the existence of mechanical surface tension γ. If we now turn to the wetting phenomenon and Eqs. (26) and (27) where γ is not in sight, then the question arises: is there a mechanochemical effect of the sign of deformation in wetting phenomena? Research in this direction was started in [105] with the wetting of single-crystal silicon plates with water drops. Statistical analysis revealed an increase in the contact angle by 1° on the convex side of the curved plate, but the effect of the sign of the deformation was not studied. In this case, rather large drops (1–2 mm in size) were used, which were already distorted to some extent by the gravitational field. A complete study of the mechanochemical effect of the

Table 1. Values of contact angles

Plate material	Molarity of KCl solution	Observed contact angle θ, deg		
		on the convex side	on the concave side	no deformation
Optical glass K-8	10^{-4}	18±0.60	13±0.53	15±0.32
	10^{-3}	22±1.10	15±0.92	16±0.61
	10^{-2}	33±1.70	30±0.82	31±1.12
Cover glass for microscopy	10^{-4}	15±1.36	11±0.66	13±1.05
	10^{-3}	16±1.12	12±1.08	15±0.64
	10^{-2}	20±1.09	16±1.39	18±0.71

sign of deformation in wetting phenomena was carried out in [118], which should be considered the publication of the discovery. Wetting was observed when small (less than 0.7 mm) bubbles were deposited on the surface of curved glass plates placed in an aqueous solution of KCl. Glass samples of two types were used: K-8 optical glass and a cover glass for microscopy. The replacement of pure water with an electrolyte solution was carried out to improve the accuracy of measurements. The fact is that a film is formed between the bubble and the solid surface, the width of which for pure water is maximum, and for the electrolyte solution it decreases with increasing ionic strength of the solution. The obtained values of the contact angles are presented in Table 1. They clearly fix the presence of the mechanochemical effect of the sign of deformation in the phenomena of wetting: on a convex surface, the contact angle is always greater, and on a concave one, it is less than on an undeformed surface.

To explain the described phenomenon, the following theory was formulated [118]. The classical Dupre equation is known, which defines the work of adhesion (more precisely, the work of separation) of contiguous phases as

$$W = \sigma^{SV} + \sigma^{LV} - \sigma^{SL}, \qquad (88)$$

where, as in the Young equation (26), σ is the thermodynamic surface tension, double superscripts symbolize the types of surfaces. In combination with Eq. (26), Eq. (88) gives

$$W = \sigma(1 + \cos\theta), \qquad (89)$$

where $\sigma \equiv \sigma^{LV}$ is the usual surface tension of the liquid. The latter is always known, and therefore Eq. (89) uniquely relates the work of adhesion to the contact angle.

Now let us talk about the work of adhesion. Obviously, it is the higher, the greater the two-dimensional density of the number of molecules in a solid monolayer. When the surface monolayer is stretched, the two-dimensional density of molecules decreases in the stretching direction, but increases in the mutually perpendicular direction. However, according to Poisson's ratio, this increase only partially compensates for the decrease in density in the direction of stretching. As a result, the two-dimensional density of the number of molecules in the surface monolayer decreases with tension, and, consequently, the work of adhesion W also decreases. Similar arguments for two-dimensional compression of the monolayer lead to the opposite result: when the surface monolayer is compressed, the work of adhesion increases. Turning now to Eq. (89), we can conclude that under uniaxial stretching of the surface of a solid body, cos θ decreases, while the contact angle θ increases. Accordingly, under uniaxial compression, cos θ increases, and the contact angle θ decreases. When a rigid plate is bent, its convex side is in stretching, and the concave side is in compression. Then we can say that the contact angle on the convex side of the plate should be greater, and on the concave side, less than on the undeformed surface. In other words, the wettability of a solid on the concave side of the plate is better than on the convex one. The data of Table 1 are fully consistent with this conclusion.

7. OTHER NEW PHENOMENA

7.1. Strong Dependence of the Contact Angle on the Pressure in the Liquid

Along with temperature, pressure is one of the main parameters of the state of liquids, but the interest in the temperature dependence is immeasurably greater than in the dependence on pressure. This is due to the fact that
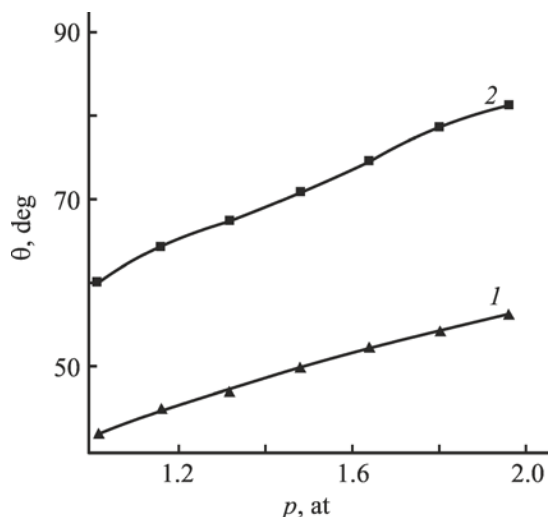
Fig. 10. Dependence of contact angle θ on water pressure p for a bubble on a polished surface of pure silicon (curve *1*) and on it after slight hydrophobization (curve *2*) [120].

liquids already have a rather high (about 10^4 atm) internal pressure, and therefore the use of ordinary pressures (of the order of several atmospheres) in them (including surface layers) does not change anything. In other words, the pressure dependence of some property of a liquid is uninteresting, because it is negligible. And now let me quote [119]: "The discovery of large effects here would be a sensation, but this is precisely what is reported in this paper devoted to the study of the contact angle of a bubble in a liquid when it sticks to the vessel wall. It was found that a change in the pressure of the liquid in the range from one to two atmospheres shifts the contact angle by values that go far beyond the limits of errors. To illustrate, we present Fig. 10 from a subsequent publication [120], where a 15°–20° change in the contact angle of water on silicon surfaces is recorded with an increase in water pressure by 1 atm.

To explain this effect, two thermodynamic relations are needed: the Young and the Gibbs adsorption equations. Under experimental conditions, all quantities in Eq. (27) except for σ_{SV} and $\cos\theta$ are almost constant, so that the change of $\cos\theta$ can be determined from the change in σ_{SV}. As already noted, when a bubble lands on a solid surface inside a liquid, a thin film of liquid (in our case, water) remains at the boundary SV. No one forbade considering it as an adsorption film of water on the surface SV, to which the Gibbs adsorption equations can be applied. Referring to Eq. (47) and assuming a rigid body to be non-deformable, we arrive at the relation

$$d\sigma_{SV} \approx -\Gamma d\mu, \qquad (90)$$

where Γ and μ are adsorption and chemical potential of water. At a constant temperature, the Gibbs–Duhem equation for a one-component liquid gives

$$dp = \rho d\mu, \qquad (91)$$

where ρ is the density of the liquid. Due to the low compressibility of the liquid far from the critical point, the value of ρ can be considered almost constant, and the values of dp and $d\mu$ are proportional to each other according to Eq. (91). After substituting Eq. (91) into Eq. (90), we obtain

$$d\sigma_{SV} \approx -\tau dp, \qquad (92)$$

where τ is the thickness of the wetting film due to the relation $\tau \approx \Gamma/\rho$. From Eq. (92) it can be seen that with increasing pressure in the liquid, the thermodynamic surface tension of the solid decreases. According to the Young equation, the cosine of the contact angle decreases, and the angle itself increases, which is observed in the experiment. Thus, Eq. (92) already gives a qualitative explanation of the data obtained.

7.2. Temperature Pinning of a Sessile Bubble

"Pinning" is a relatively new term in colloidal science, referring to the sudden stop of a three-phase contact line when a droplet spreads or a bubble propagates along the surface of the solid on which they are located. The nature of pinning is not completely clear yet. Perhaps it is related to the substrate relief (surface roughness or mosaic), but this requires a special study. For a macroscopic, but small (less than 1 mm in size if we are talking about a bubble in water) sessile bubble, the influence of the gravitational field on its shape can be neglected and considered as a spherical segment. Then the geometry defines the contact angle θ as

$$\theta = 2\arctan\frac{r}{h}, \qquad (93)$$

where r is the radius of the three-phase contact line of the bubble and h is its height (Fig. 11). In the process of bubble growth, all quantities in Eq. (93) change smoothly. If r becomes constant (which is a manifestation of pinning), then the apparent radius of the three-phase contact line gas-liquid-solid ceases to be a state parameter
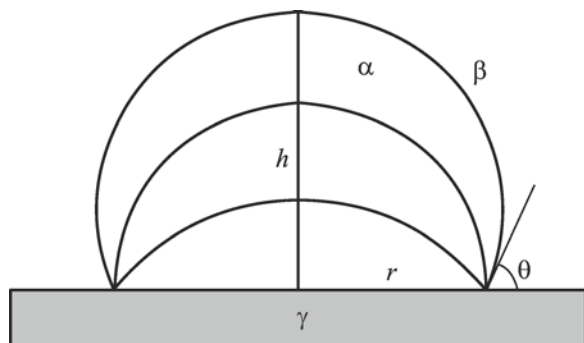
Fig. 11. Pinning of a sessile bubble: h and r are the height of the bubble and the radius of its base, θ is the contact angle. Phase designation: α—gas, β—liquid, γ—solid.

Fig. 12. Temperature dependence of the bubble contact angle θ at the quartz–water interface [123].

for some time. The line freezes in place, while the other parameters of the bubble continue to change along with its volume. In this case, the contact angle decreases with increasing bubble size (Fig. 11).

To study pinning in bubbles, the size of a bubble is artificially increased by pumping gas into it through a microsyringe [121]. We used a non-contact technique associated with an increase in temperature, when the bubble inflates by itself. The phenomenon that was observed here we called temperature pinning [122]. We also encountered temperature pinning in [123], although it was carried out with a slightly different goal: experimental verification of the temperature dependence of the contact angle predicted in [124]. In particular, it was shown there that, on a hydrophilic surface, the contact angle should increase with increasing temperature, while on a hydrophobic surface, on the contrary, it should decrease. As an example, Fig. 12 shows the temperature dependence of the bubble contact angle θ at the quartz–water interface. The range of the contact angle is such that the hydrophilicity of the surface is immediately visible, and for this type of surfaces, work [124] predicts an increase in the contact angle with temperature. Indeed, most of the points on the graph meet this criterion. However, the first three points demonstrate the opposite dependence, which raises questions. They are removed when we look at Fig. 13 is the result of a parallel measurement of the line radius of a three-phase contact in the same system.
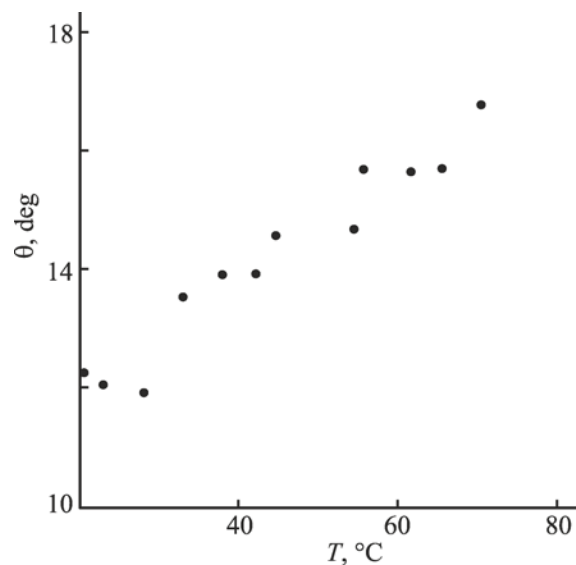
It can be seen that just the first three points correspond to temperature pinning, which was not envisaged in theory (the surface was assumed to be ideally smooth).

In conclusion, we give an example with a hydrophobic surface, on which the initial contact angle of water was 95° (Fig. 14). By connecting the experimental points with a line in order to better see the horizontal sections, we find them in a triple number. Thus, summing up our data, we can conclude that temperature pinning occurs very often and finds various manifestations.

8. *J*-POTENTIAL IS THE THERMODYNAMIC POTENTIAL OF MINE

As is known, in thermodynamics, characteristic functions and thermodynamic potentials are distinguished among the most important quantities. For the former, fundamental equations are written, with the help of which one can construct the entire equilibrium thermodynamics and find all thermodynamic quantities by differentiating the characteristic functions. As for the thermodynamic potentials, under certain conditions (with the constancy of their characteristic variables), their change gives the work of the process. Thermodynamics existed as a science even before Gibbs, but was the thermodynamics of cycles, while Gibbsian thermodynamics is the thermodynamics of potentials. You need to work with it in the following way: look at the conditions under which the process takes place, select the appropriate characteristic variables and
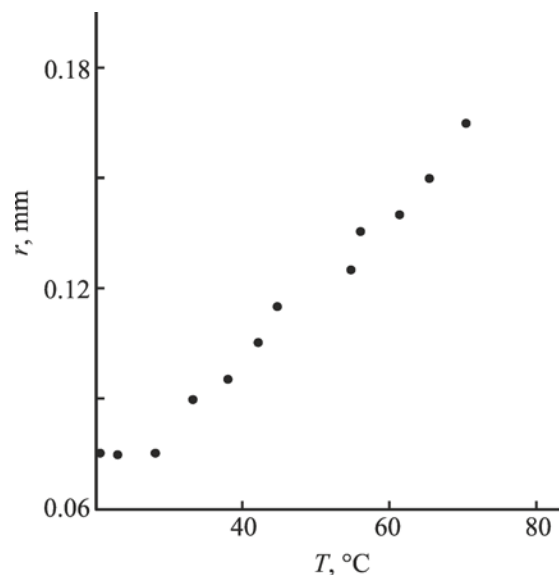
Fig. 13. Temperature dependence of the radius r of the base of a sessile bubble on a hydrophilic quartz surface. The first points of the curve demonstrate temperature pinning [123].
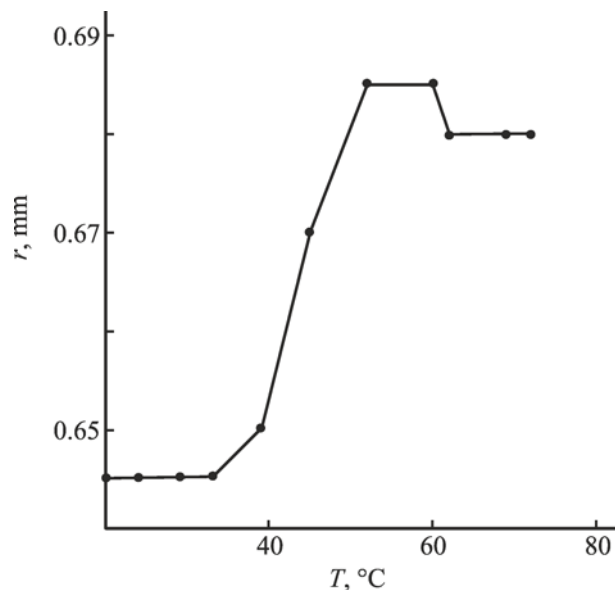

Fig. 14. Temperature dependence of the radius of the base of a sessile bubble on a hydrophobic surface with an initial angle of 95°. Three horizontal sections—temperature pinning [122].

make calculations using their thermodynamic potential. It already follows from this that there should be several thermodynamic potentials. The more of them, the better thermodynamics is developed.

8.1. Thermodynamic Potentials for Closed Systems

Each thermodynamic potential is a characteristic function, but not vice versa. For example, entropy is a characteristic function, but by no means a thermodynamic potential (it does not even have the dimension of energy). All thermodynamic potentials are derivatives of internal energy. It is the main thermodynamic potential U, for which the equilibrium fundamental equation is written as a joint formulation of the first and second principles of thermodynamics [125]

$$\delta U = T\delta S + \oint_{(A)} (\mathbf{P} \cdot \delta\mathbf{u})dA + \delta W, \qquad (94)$$

where S is the entropy of the system, T is the absolute temperature, $\mathbf{P}$ is the local vector of the external force applied to the unit of the external surface of the system (such a force is called stress), $\mathbf{u}$ is the local displacement vector of the surface (the dot means the scalar product of these two vectors, which gives the elementary work of displacement of a unit surface), A is the area of the

surface, and (A) is the symbol of the most closed surface of the system over which the integration is performed. The second term on the right side of Eq. (94) reflects the mechanical work of external contact forces. If the system is surrounded by a homogeneous external environment (for example, the atmosphere) with pressure p (pressure and stress are always opposite in sign), then it reduces to the well-known expression $-pdV$, where V is the volume of the system. The third term reflects any other work. Thus, the entire Eq. (94) conveys the meaning of the first law of thermodynamics, which consists in the fact that an increase in the energy of the system is achieved by the supply of heat and the performance of work on the system by external bodies. From Eq. (94) follows the condition (N_i is the number of molecules of component i in the system) [125]

$$\delta U = \delta W \ (\delta S = 0, \delta\mathbf{u} = 0, \delta N_i = 0), \qquad (95)$$

which indicates that the internal energy is a thermodynamic potential, provided that the entropy, the boundaries of the system and the quantities of all components are fixed. What happens if these conditions are not met? Will there be a change in energy? Of course, it will and will remain an important characteristic of a substance, but at the same time it will no longer reflect the operation of the process and in this respect will lose its defining

significance. Energy is not always important, but work is always important.

Let us briefly recall other thermodynamic potentials for closed systems. The free energy F (once the Helmholtz free energy, but the name has long since fallen out of the name) is defined as

$$F \equiv U - TS \tag{96}$$

(the TS term qualifies as bound energy). From Eqs. (94) and (96), we arrive at the expression

$$\delta F = -S\delta T + \oint_{(A)} (\mathbf{P} \cdot \delta\mathbf{u})dA + \delta W, \tag{97}$$

and the condition

$$\delta F = \delta W \ (\delta T = 0, \delta\mathbf{u} = 0, \delta N_i = 0), \tag{98}$$

whence it follows that free energy is a thermodynamic potential at constant temperature, system boundaries, and amounts of all components. As a thermodynamic potential, free energy is more practical than energy, since isothermal processes are easier and more often to deal with than adiabatic ones.

Let us move on to the Gibbs energy. At the dawn of my studies in thermodynamics, it was called the "Gibbs thermodynamic potential" [69] or "Gibbs free energy" and was defined for homogeneous fluid systems as

$$G \equiv F + pV \equiv U - TS + pV. \tag{99}$$

Now, turning to the case of an arbitrary system, we can define the Gibbs energy as [125]

$$G \equiv U - TS - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u})dA. \tag{100}$$

From Eqs. (97) and (100), we find

$$\delta G \equiv -S\delta T - \oint_{(A)} (\delta\mathbf{P} \cdot \mathbf{u})dA + \delta W. \tag{101}$$

From here, the condition follows

$$\delta G = \delta W \ (\delta T = 0, \delta\mathbf{P} = 0, \delta N_i = 0) \tag{102}$$

characterizing the Gibbs energy as a thermodynamic potential at constant temperature, all external forces applied to the system, and the amounts of all components. If the only external force is atmospheric pressure, then with its constancy (within the laboratory experiment)

and a given temperature, the Gibbs energy in the form of Eq. (99) is the only one suitable for calculating work. This is the most popular thermodynamic potential.

What remains is the enthalpy H, commonly known as the heat function. However, as was shown [125], it can also play the role of a thermodynamic potential. For fluid systems, enthalpy is defined as

$$H \equiv U + pV. \tag{103}$$

By analogy with Eq. (100), one can determine the enthalpy for a body of any nature and with an arbitrary distribution of external forces on it as

$$H \equiv U - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u})dA. \tag{104}$$

Varying Eq. (104) and substituting Eq. (94) there, we find the relation

$$\delta H \equiv T\delta S - \oint_{(A)} (\delta\mathbf{P} \cdot \mathbf{u})dA + \delta W, \tag{105}$$

from which the condition follows (recall that we are talking about a closed system)

$$\delta H = \delta W \ (\delta S = 0, \delta\mathbf{P} = 0, \delta N_i = 0). \tag{106}$$

Condition expressed in Eq. (106) indicates that enthalpy can indeed be a thermodynamic potential when entropy, all external forces and amounts of all components are fixed.

8.2. Open Systems. Large Thermodynamic Potential

In open systems, another type of work appears, the transfer of matter from the environment to the system under consideration and vice versa, which obviously affects the internal energy of the system. In addition, thanks to the exchange of matter, a mechanism appears for influencing chemical potentials and creating states with fixed chemical potentials. However, only fluid systems are accessible to such influence, in which the free migration of molecules ensures the equalization of chemical potentials. For an open fluid system, Eq. (94) takes the form

$$\delta U = T\delta S - p\delta V + \sum_i \mu_i \delta N_i + \delta W, \tag{107}$$

where μ_i is the chemical potential of component i. We still see that condition expressed in Eq. (95) (with softening of

the constancy of **u** by the constancy of the volume V) is satisfied, and the internal energy can be a thermodynamic potential only for a closed system.

All four described thermodynamic potentials are available in Gibbs' work "On the Equilibrium of Heterogeneous Substances" (1876) [83, 84]. To move on to the fifth, we need to remember that after this work, Gibbs took up statistical mechanics, where closed and open systems were also considered. The latter corresponds to the thermodynamic potential

$$\Omega \equiv U - TS - \sum_i \mu_i N_i \equiv F - \sum_i \mu_i N_i. \qquad (108)$$

Since this function is directly related to the Gibbs grand canonical distribution, I once began to call it the "grand" thermodynamic potential, although I had never seen such a name before. Perhaps someone did it before, but what does it matter? After all, coming up with a new name (I am afraid that "Gibbs energy" is also my invention) does not mean making a discovery. It is important that the term has taken root (at least in the St. Petersburg thermodynamic school).

Varying Eq. (108) and substituting Eq. (107) there, we arrive at the expression

$$\delta\Omega = -S\delta T - p\delta V - \sum_i N_i \delta\mu_i + \delta W. \qquad (109)$$

Equation (109) implies the condition

$$\delta\Omega = \delta W \ (\delta T = 0, \ \delta V = 0, \ \delta\mu_i = 0) \qquad (110)$$

showing that the grand thermodynamic potential is suitable for calculating work at constant temperature, volume, and chemical potentials of the system components. When introducing the grand thermodynamic potential, it was assumed that all chemical potentials would be fixed, but a more subtle approach is also possible. Thus, it may turn out that some of the components of the system are in a solid state, and for them the fixing of chemical potentials is impossible, while the other part of the components freely migrates in the system, and their chemical potentials can be controlled. For such cases, the so-called "hybrid" thermodynamic potentials are introduced, which do not have special names, but work properly (see below).

All five of these thermodynamic potentials are at the same time characteristic functions of the same variables, when fixing which they give the work of the process. Their total differentials (we write them for fluid systems

and in the absence of other external forces, except for pressure) form a system of fundamental equations:

$$dU = TdS - pdV + \sum_i \mu_i dN_i, \qquad (111)$$

$$dF = -SdT - pdV + \sum_i \mu_i dN_i, \qquad (112)$$

$$dG = -SdT + Vdp + \sum_i \mu_i dN_i, \qquad (113)$$

$$dH = TdS + Vdp + \sum_i \mu_i dN_i, \qquad (114)$$

$$d\Omega = -SdT - pdV - \sum_i N_i d\mu_i. \qquad (115)$$

Integration of fundamental equations (111)–(115) for a given physical state of the system gives explicit expressions for the thermodynamic potentials themselves (integral fundamental equations):

$$U = TS - pV + \sum_i \mu_i N_i, \qquad (116)$$

$$F = -pV + \sum_i \mu_i N_i, \qquad (117)$$

$$G = \sum_i \mu_i N_i, \qquad (118)$$

$$H = TS + \sum_i \mu_i N_i, \qquad (119)$$

$$\Omega = -pV. \qquad (120)$$

The above fundamental equations correspond to the Gibbs equilibrium principle, formulated as the principle of maximum entropy or minimum of thermodynamic potentials. For fluid systems, this is expressed by a set of equivalent conditions [125]:

$$(dU)_{S,V,N_i} = 0, \qquad (121)$$
$$(dF)_{T,V,N_i} = 0, \qquad (122)$$
$$(dG)_{T,p,N_i} = 0, \qquad (123)$$
$$(dH)_{S,p,N_i} = 0, \qquad (124)$$
$$(d\Omega)_{T,V,\mu_i} = 0. \qquad (125)$$

In terms of energy and free energy, the principle of equilibrium is also applicable to solids, provided that the constancy of volume is replaced by the invariance of the boundaries of the system in all directions.

8.3. Modified (Hybrid) Thermodynamic Potentials

Now let us look at the simplest expressions for the five known thermodynamic potentials (116)–(120)

and note that the introduction of each thermodynamic potential is associated with the removal of one or more terms in Eq. (116) for energy. If the terms are of the same type (for example, terms with chemical potentials), and only some of them are removed, then modified (hybrid) thermodynamic potentials are formed. They are especially characteristic of a solid body [73], where there are always immobile components (forming a lattice), but mobile components can also be present (subscripts j and i, respectively). For example, the expression for the free energy of an isotropic (not to deal with tensor expressions) amorphous (with a disordered lattice) solid has the form

$$F = -pV + \sum_j \mu_j N_j + \sum_i \mu_i N_i. \qquad (126)$$

We introduce a new thermodynamic potential according to the scheme

$$\tilde{F} \equiv F - \sum_i \mu_i N_i = -pV + \sum_j \mu_j N_j \equiv \Omega + \sum_j \mu_j N_j \equiv \tilde{\Omega}. \quad (127)$$

Modified free energy $\tilde{F}$ is a hybrid thermodynamic potential that has the properties of free energy with respect to immobile components of a solid body and the properties of grand thermodynamic potential with respect to mobile components. This function can also be called the modified grand thermodynamic potential and denoted $\tilde{\Omega}$, as shown in Eq. (127).

8.4. Definition of J-Potential

Having talked about the existing five thermodynamic potentials and their modifications, we thereby determined the background against which the discovery of the sixth took place [126, 127]. All the above relationships refer to a homogeneous (single-phase) fluid system. Going down in the series of Eqs. (116)–(120), we arrive at Eq. (120) for grand thermodynamic potential with only one term $-pV$. It seems to be a limit. After all, if we define a certain thermodynamic J-potential as

$$J \equiv \Omega + pV, \qquad (128)$$

then we get zero. But this is only for homogeneous systems! This is where the time has come to change the prevailing views. It was not stipulated anywhere, but it was always implied that any thermodynamic potential should be applicable to homogeneous systems. The J-potential does not satisfy this condition, but if it is good for heterogeneous systems, then why not use it? In the

thermodynamics of surfaces, there are no homogeneous systems at all, because where there are surfaces, there must be at least two phases. Therefore, one can say that the J-potential is, as it were, specially created for colloid science.

Definition expressed by Eq. (128) is applicable to fluid capillary systems whose fundamental equation for grand thermodynamic potential has the form

$$d\Omega = -SdT - \sum_i N_i d\mu_i - pdV + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t, \quad (129)$$

where $\gamma^s = \sigma^s$ is the surface tension for a surface with an area A^s and $\tau^t = \kappa^t$ is the linear tension for a line of length L^t (s and t are serial numbers). Differentiating Eq. (128) with substituting Eq. (129), we obtain a fundamental equation for J-potential

$$dJ = -SdT - \sum_i N_i d\mu_i + Vdp + \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t, \quad (130)$$

where, we recall, p is the external pressure for the system under consideration. Thermodynamic experts will say that the first three terms on the right-hand side of Eq. (130) should cancel each other out according to the Gibbs-Duhem equation, but this is true only when all surfaces are flat and the pressure is the same everywhere. In this case, or at constant temperature, external pressure, and chemical potentials, Eq. (130) simplifies to the form

$$dJ = \sum_s \gamma^s dA^s + \sum_t \tau^t dL^t, \qquad (131)$$

which is very convenient for the thermodynamics of surfaces. Integrating Eq. (131) with constant intensive parameters gives the integral fundamental equation for J-potential

$$dJ = \sum_s \gamma^s A^s + \sum_t \tau^t L^t, \qquad (132)$$

the very appearance of which confirms the importance of J-potential for colloidal science.

To formulate the principle of equilibrium in terms of J-potential, imagine that the entire heterogeneous system as a whole is surrounded by a homogeneous medium with pressure p, which is thus the external pressure for our system. Then, for grand thermodynamic potential, the principle of equilibrium is formulated in the form of Eq. (125), whence, taking into account Eq. (128), we find

$$(dJ)_{T,p,\mu_i} = 0. \tag{133}$$

This is the equilibrium principle for J-potential in a fluid system. In particular, in the presence of flat surfaces, the substitution of Eq. (131) into Eq. (133) gives

$$\sum_s \gamma^s dA^s + \sum_t \tau^t dL^t = 0 \tag{134}$$

for all surfaces and lines that do not cross the boundary of the system.

The above equations were related to fluid systems. In the most general case, including solids, J-potential can be defined as follows:

$$J \equiv \Omega - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA, \tag{135}$$

where $\mathbf{P}$ is the external force per unit area A of the surface of the system (A) as a function of the position on the surface, $\mathbf{u}$ is the local displacement vector of the surface; integration is performed over the entire closed surface of the system. Note that the tensions of surfaces and lines crossing the boundary of the system themselves become external forces, but in order to avoid misunderstandings (up to J-potential turning to zero even for heterogeneous systems), it is better to agree from the very beginning that such forces are not included in the value of $\mathbf{P}$, although a different approach is possible in a number of special problems. The presence of external forces leads to the formation of a stress tensor field inside the system. Mathematically, both formalisms are related as

$$\oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA = \iiint_{(V)} (\hat{E} : \hat{e}) dx dy dz, \tag{136}$$

where $\hat{e}$ is the strain tensor, and the colon means the biscalar product of tensors.

In the case of a solid body with one immobile (subscript j) and mobile (subscript i) components, the expression for grand thermodynamic potential Ω in Eq. (135) can be written as [128]

$$\Omega \equiv F - \sum_i \mu_i N_i - \mu_j^\beta N_j = F - \sum_i \mu_i N_i - \mu_{j(nn)}^\alpha N_j, \tag{137}$$

where superscript α refers to the solid phase, and β refers to the real or imaginary fluid phase in equilibrium with the α phase. The value μ_j^β is the chemical potential of component j in solution, while $\mu_j^\alpha{}_{(nn)}$ is the component of

the chemical potential tensor of component j in the solid phase that is normal to the surface. These two chemical potentials are related by the Gibbs equilibrium condition for the flat boundary of a macroscopic solid with a liquid

$$\mu_{j(nn)}^\alpha = \mu_j^\beta. \tag{138}$$

Recall that, as was shown in [89], in accordance with Eq. (65), equality Eq. (138) is also valid for nanoparticles if its left-hand side refers to the surface monolayer of the particle. The equilibrium principle for J-potential (Eq. (135)) is written as

$$(\delta J)_{T,P,\mu_i,\mu_{j(nn)}} = 0. \tag{139}$$

An essential feature of the definition expressed in Eq. (137), and hence the definition of J-potential as Eq. (135), is the binding to a certain surface through which a solid can dissolve or evaporate. If a body is in an anisotropic state and has several surfaces of different orientations (and, possibly, of different nature), then there will be several definitions of Ω, and, consequently, J-potential (Eq. (135)) will be defined ambiguously. This inconvenience can be circumvented by introducing a hybrid J-potential.

8.5 Hybrid J-Potential

Hybrid J-potential (denoted as $\tilde{J}$) can be defined as

$$\tilde{J} \equiv \tilde{\Omega} - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA, \tag{140}$$

where $\tilde{\Omega}$ is the hybrid function shown in Eq. (127), which plays the role of grand thermodynamic potential only in relation to mobile components, and in relation to immobile components of a solid, it acts as free energy. Accordingly, the components of the mass displacement tensor of the immobile component $\hat{N}_j$ [43], rather than the chemical potential tensor, act as variables. In comparison with Eq. (139), the equilibrium principle is formulated for the hybrid J-potential as

$$(\delta \tilde{J})_{T,P,\mu_i,\hat{N}_j} = 0. \tag{141}$$

The fundamental equations for $\tilde{J}$ are easily deduced from the equations for free energy. In the case of a homogeneous phase α in an anisotropic state, we have [42]

$$dF^\alpha = -S^\alpha dT + V^\alpha(\hat{E}^\alpha : d\hat{e}^\alpha) + \mu_j^\alpha : d\hat{N}_j^\alpha + \sum_i \mu_i dN_i^\alpha. \quad (142)$$

Integration of Eq. (142) along any of the principal directions k gives

$$F^\alpha = E_k^\alpha V^\alpha + \mu_{j(k)}^\alpha N_j^\alpha + \sum_i \mu_i N_i^\alpha. \quad (143)$$

If we now simplify the definition given by Eq. (140) to the form (taking into account the equilibrium condition $P = E_k$)

$$\tilde{J} \equiv \tilde{\Omega} - PV = \tilde{\Omega} - E_k V, \quad (144)$$

then, from Eqs. (140), (143), and (144), we obtain

$$\tilde{J}^\alpha = \mu_{j(k)}^\alpha N_j^\alpha. \quad (145)$$

This shows that hybrid J-potential of the bulk phase is nonzero. Using now Eqs. (142) and (144), we write the fundamental equation of the bulk phase in terms of hybrid J-potential:

$$d\tilde{J}^\alpha = -S^\alpha dT + V^\alpha(\hat{E}^\alpha - \hat{I}E_k^\alpha) : d\hat{e}^\alpha$$
$$- V^\alpha dP + \hat{\mu}_j : d\hat{N}_j - \sum_i N_i d\mu_i. \quad (146)$$

Now let us see how the Gibbs surface excess of hybrid J-potential looks like (we will add an overline to denote excess surface quantities). Turning to the interfacial surface, first of all, we note that, in view of the zero excess of the last term in Eq. (144), the excesses of the functions $\tilde{J}$ and $\tilde{\Omega}$ coincide: $\overline{\tilde{J}} = \overline{\tilde{\Omega}}$. The relations for $\overline{\tilde{\Omega}}$ are well studied [42] and lead to the equation

$$\overline{\tilde{J}} = \overline{\tilde{\Omega}} = \sigma A, \quad (147)$$

which, however, is satisfied only if the equimolecular surface with respect to the immobile component is taken as a dividing surface Differentiating Eq. (147) and using the generalized Gibbs adsorption equation for σ (47), we obtain the fundamental equation for the surface hybrid J-potential

$$d\overline{\tilde{J}} = -\overline{S}dT + \sigma dA + A(\hat{\gamma} - \sigma\hat{I}) : (d\hat{e}^\sigma - d\hat{N}_j/N_j) - \sum_i \overline{N}_i d\mu_i. \quad (148)$$

Passing from surfaces to lines and taking the second excess along the surface (the second line from the top), for the linear hybrid J-potential, we find the fundamental equation

$$d\overline{\overline{J}} = -\overline{\overline{S}}dT + \kappa dL + (\tau - \kappa)dL - \sum_i \overline{\overline{N}}_i d\mu_i, \quad (149)$$

where, we remind, γ is mechanical, and σ is thermodynamic linear tension. This completes the presentation of the new thermodynamic potential J. We now give examples of the practical use of J-potential, illustrating its usefulness.

8.6. Neumann and Gibbs Equations

As the simplest example of the application of J-potential, consider the known equilibrium conditions for surfaces that meet on the same interface line. In terms of mechanical surface tension γ_k (k is the surface number), one of them is expressed by the vector Neumann equation

$$\sum_k \boldsymbol{\gamma}_k = 0, \quad (150)$$

which is trivially treated as the equilibrium of the force vectors applied to the line. But here the question immediately arises: how can one write a vector equation when surface tension is not a vector, but a tensor? This contradiction is easily removed. The point is that each surface has a direction specified (along the normal to the line) by a unit vector $\mathbf{v}_k$, and the scalar product [42]

$$\hat{\gamma} \cdot \mathbf{v}_k = \boldsymbol{\gamma}_k \quad (151)$$

gives the real force acting on the line from the k-th surface, and this force is a vector. The condition expressed in Eq. (150) is always true for fluid systems (if the surface tensions of the surfaces are the same, then the number of the latters on one line cannot be more than three, as it turns out in foams), but if there are solid surfaces on the left side of Eq. (150), internal stresses arise in solids [42].

In terms of thermodynamic surface tension σ, the equilibrium condition is given by the Gibbs equation, but since we are talking about different physical quantities, the Neumann and Gibbs equations are different relationships. But surprisingly, the Gibbs equation is also a vector, although σ is a purely scalar quantity. True, Gibbs indicated this in verbal form and did not write a single vector. That was the second case in the author's
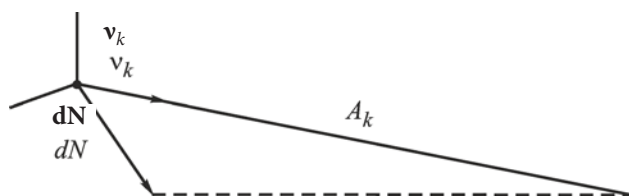
Fig. 15. Cross section of interfaces (looking like lines) intersecting on the same interface (shown by a large dot): $\mathbf{v}_k$ is unit vector indicating the direction of the surface k, $\mathbf{dN}$ is displacement vector of the interface (the new position of the surface k is shown by a dotted line).
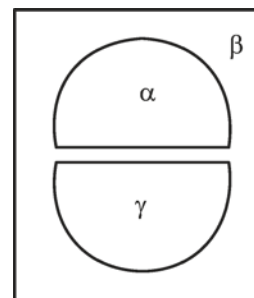

Fig. 16. Flat thin film between two bubbles in a liquid: α—external phase (air), β—mother phase.

life when he had to dress Gibbs' verbal statements in mathematical clothes (the first case was associated with the reduced Le Chatelier–Brown principle, as described above). Let us see what happens when using the hybrid J-potential.

If the surfaces are flat and the only external force is atmospheric pressure, then from Eqs. (141), (146), and (148), we obtain

$$d\tilde{J} = \sum_k \sigma_k dA_k = 0 \qquad (152)$$

for virtual changes that do not deform surfaces, but only change their position at a fixed line length. It is curious that Gibbs proceeded from the same expression, but he extracted it from more complex expressions (the operation is not always unambiguous). There is no need for this in the presence of J-potential. The virtual change we are considering is the displacement of the interface parallel to itself (Fig. 15). If $\mathbf{dN} = \mathbf{n}dN$ is the line displacement vector along the normal ($\mathbf{n}$ is the unit displacement vector), then the change in the area of the kth surface with direction $\mathbf{v}_k$ is

$$dA_k = -(\mathbf{v}_k \cdot \mathbf{dN}) = -(\mathbf{v}_k \cdot \mathbf{n})dN. \qquad (153)$$

Substituting Eq. (42) in Eq. (41) yields

$$(\mathbf{n} \cdot \sum_k \sigma_k \mathbf{v}_k)dN = 0. \qquad (154)$$

Since the displacement dN is arbitrary, the condition expressed ib Eq. (43) can only be satisfied for

$$(\mathbf{n} \cdot \sum_k \sigma_k \mathbf{v}_k) = 0. \qquad (155)$$

If the direction of displacement $\mathbf{n}$ can be arbitrary, then, from Eq. (155), it follows

$$\sum_k \sigma_k \mathbf{v}_k = 0. \qquad (156)$$

This is the vector Gibbs equation (formulated by him only verbally). In particular, it also holds for fluid systems, when passing, thus, to the Neumann equation. We emphasize, however, that Eq. (155) is a more general and more important relation than the vector equation (156). For example, a particular case of Eq. (155) is the classical Young equation [127].

8.7. J-POTENTIAL IN THE THERMODYNAMICS OF THIN FILMS [129]

We have already dealt with thin films and their disjoining pressure (Eq. (11)) in Chap. 2. The state of modern thermodynamics of thin films (it goes beyond the limits of Gibbs thermodynamics) was presented in [3, 130, 131]. But now we are interested in another question: what phases are typical for a system with a thin film? Figure 16 depicting a flat thin film between two bubbles (or drops of other liquids) in a liquid indicates two phases: the phase α external to the film and the mother phase of the film β. Note that with a certain choice of system boundaries, the phase β can also be interpreted as external, so that both pressures $p^\alpha = p^\gamma$ and p^β (the difference between them is precisely the disjoining pressure of the film Π) can be considered as external pressures when defining J-potential. In this regard, we can introduce a more general definition

$$J \equiv \Omega + p'V, \qquad (157)$$

or, for hybrid potential,

$$\tilde{J} \equiv \tilde{\Omega} + p'V, \qquad (158)$$

where p' is some chosen pressure. This may be external pressure relative to the heterogeneous system as a whole, pressure in one of the phases of the heterogeneous system, or any other pressure. In the version presented by Eq. (157), the term J-potential already denotes a whole series of potentials of a certain type. In the classical approach, p' is assumed to be equal to the external pressure p^α ($p' = p^\alpha$). For brevity, we will call this type of J-potential classical (designation J_c), and all other types derived from Eqs. (157) and (158) are special J-potentials (designation J_s).

When formulating the J-potential in a system with a thin film, one must also take into account which Gibbs method of consideration is used. There are two such methods [130, 131] (let us conditionally mark them as A and B). In the first, only one dividing surface is used and the thin film is treated as an interface. Film tension is interpreted as surface tension $\sigma^{\alpha\gamma}$. Method B uses two dividing surfaces $\alpha\beta$ and $\gamma\beta$ with tensions $\sigma^{\alpha\beta}$ and $\sigma^{\gamma\beta}$. The distance between the dividing surfaces defines the film thickness H, and the relationship between these values is given by the known equation [31]

$$\sigma^{\alpha\gamma} = \sigma^{\alpha\beta} + \sigma^{\gamma\beta} + \Pi H. \tag{159}$$

We now give a summary of the results.

1. $p' = p^\alpha$, A.

$$J_c = \sigma^{\alpha\gamma} A^{\alpha\gamma}, \tag{160}$$

$$dJ_c = -\bar{S}dT - \sum_i \bar{N}_i d\mu_i + \sigma^{\alpha\gamma} dA, \tag{161}$$

$$\tilde{J}_c = \mu_m N_m^\alpha + \mu_n N_n^\gamma + \sigma^{\alpha\gamma} A, \tag{162}$$

$$d\tilde{J}_c = -SdT - \sum_i N_i d\mu_i + \mu_m dN_m^\alpha + \mu_n dN_n^\gamma + Vdp^\alpha + \sigma^{\alpha\gamma} dA. \tag{163}$$

2. $p' = p^\alpha$, B.

$$J_c = \Pi V^\beta + (\sigma^\alpha + \sigma^\gamma)A, \tag{164}$$

$$dJ_c = -\bar{S}dT - \sum_i \bar{N}_i d\mu_i + V^\beta d\Pi + (\sigma^\alpha + \sigma^\gamma)dA, \tag{165}$$

$$\tilde{J}_c = \mu_m N_m^\alpha + \mu_n N_n^\gamma + \Pi V^\beta + (\sigma^\alpha + \sigma^\gamma)A, \tag{166}$$

$$d\tilde{J}_c = -SdT - \sum_i N_i d\mu_i + \mu_m dN_m^\alpha + \mu_n dN_n^\gamma + Vdp^\alpha + (\sigma^\alpha + \sigma^\gamma)dA. \tag{167}$$

3. $p' = p^\beta$, A.

$$J_s = -\Pi V + \sigma^{\alpha\gamma} A, \tag{168}$$

$$dJ_s = -SdT - \sum_i N_i d\mu_i - \Pi dV + Vdp^\beta + \sigma^{\alpha\gamma} dA, \tag{169}$$

$$\tilde{J}_s = \mu_m N_m^\alpha + \mu_n N_n^\gamma - \Pi V + \sigma^{\alpha\gamma} A, \tag{170}$$

$$d\tilde{J}_s = -SdT - \sum_i N_i d\mu_i + \mu_m dN_m^\alpha + \mu_n dN_n^\gamma - \Pi dV + Vdp^\beta + \sigma^{\alpha\gamma} dA. \tag{171}$$

4. $p' = p^\beta$, B.

$$J_s = -\Pi(V^\alpha + V^\gamma) + (\sigma^\alpha + \sigma^\gamma)A, \tag{172}$$

$$dJ_s = -SdT - \sum_i N_i d\mu_i - \Pi dV + Vdp^\beta + (\sigma^\alpha + \sigma^\gamma)dA, \tag{173}$$

$$\tilde{J}_s = \mu_m N_m^\alpha + \mu_n N_n^\gamma - \Pi(V^\alpha + V^\gamma) + (\sigma^\alpha + \sigma^\gamma)A, \tag{174}$$

$$d\tilde{J}_s = -SdT - \sum_i N_i d\mu_i + \mu_m dN_m^\alpha + \mu_n dN_n^\gamma - \Pi dV + Vdp^\beta + (\sigma^\alpha + \sigma^\gamma)dA. \tag{175}$$

These expressions well illustrate the variety of relationships given by J-potential.

8.8. J-Potential in the Theory of Strength of Materials

It should be noted that the field of knowledge related to the strength of materials, created mainly by mechanics, is directly related to colloidal science for the direct reason that the destruction of any body is the creation of a new surface. Therefore, it is not surprising that colloid scientists have long been involved in the study of the strength of materials. In the 20th century, an outstanding contribution to this field of science was made by the school of P.A. Rehbinder by the discovery of the Rehbinder effect, adsorption decrease in strength.

As regards the theory of strength, already in the fundamental classical work of Griffith (his energy approach is close to thermodynamics) [132], the concept of surface tension was used as he understood it. The ultimate solid strength found by Griffith at brittle fracture (we denote it as E_t), is of the form

$$E_t = \left(\frac{\sigma}{bc}\right)^{1/2}, \, b \equiv \frac{\pi\nu}{2Y}, \tag{176}$$

where, in the modern interpretation, σ is the thermodynamic surface tension of the material, c is the crack depth, Y is Young's modulus and ν is Poisson's ratio. Eq. (176) can
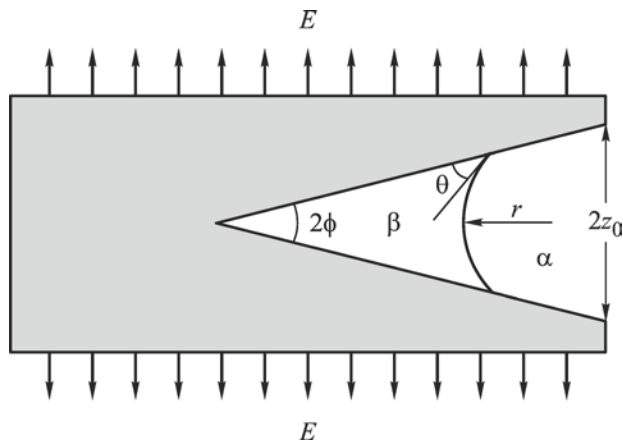
Fig. 17. A solid with a crack under stress for the case of capillary condensation: E is external stress, 2ϕ is the crack frontal angle, θ is contact angle, α is the external phase (air), β is a liquid phase in the crack nose, r is the radius of the interfacial surface $\alpha\beta$, $2z_0$ is the width of the crack mouth.

be understood in two ways: (1) if there is a crack with depth c in a body with thermodynamic surface tension σ, then external stress must be applied to destroy the body; (2) if the body is loaded with stress σ, then a crack in it can grow without destruction only up to the critical depth c, determined by Eq. (176). Modern thermodynamics of surface phenomena has introduced its own corrections into Griffith's theory [133–136]. Further development of the theory led to the creation of a whole new field, the thermodynamics of cracks [137–139]. Numerous calculations in this area for dispersion forces were recently presented in review [131].

If the crack is empty, the theory is simpler and can be constructed using any thermodynamic potentials. But if the crack is even slightly filled with foreign matter (and this can greatly affect the material strength), then a J-potential is required to build a theory. Let us explain this in more detail [139]. Let a solid body with a crack be subjected to the action of two forces: external (for example, atmospheric) pressure p^α and uniaxial loading (stress in the direction r) $E \equiv E_{rr}$, perpendicular to the mean plane of the crack (stress E is measured from the external pressure). Let there also be a foreign substance in the crack that forms the phase β (phase α is the external medium) in the form of a meniscus in the crack nose with a contact angle θ and radius r. This whole picture is shown in Fig. 17.

The corresponding value of J-potential defined in Eq. (135) (we denote it J_r) can be written as

$$J_r \equiv F + p^\alpha V - EV - \sum_i \mu_i N_i. \qquad (177)$$

The system under consideration consists of three parts: the solid body itself (we will mark it with subscript s), the external phase α, partially entering the crack, and the phase β, located in the crack nose. Let us single out from the potential its part related to the bulk phase of the solid

$$J_r^s = F^s + p^\alpha V^s - EV^s, \qquad (178)$$

and, accounting for the volume balance $V = V^s + V^\alpha + V^\beta$, we write

$$J_r = J_r^s + (p^\alpha - p^\beta)V^\beta + \sigma^\alpha A^\alpha + \sigma^\beta A^\beta + \gamma A^{\alpha\beta} + \kappa L, \qquad (179)$$

where V^α and V^β are the volumes of phases α and β, σ^α and σ^β are the macroscopic values of the thermodynamic surface tensions of the crack walls at the boundary with the α and β phases, A^α and A^β are the total contact areas of the walls with α and β phases, γ ($=\sigma^{\alpha\beta}$) is the surface tension at the boundary of the α and β phases (surface meniscus tension), $A^{\alpha\beta}$ is the meniscus surface area, κ and L are the thermodynamic linear tension and the length of the crack front line. Note that in Eq. (179), only the volume of the phase β adjacent to the crack nose remains; the volume of the phase α (which can go beyond the crack) is no longer important.

Potential J_r gives the work of the process under the condition of constant temperature, mass and external loading of the solid body, external pressure and chemical potentials of the moving components. In particular, this can be a crack growth process, which is well reflected by the differential fundamental equation

$$dJ_r = dJ_r^s + (p^\alpha - p^\beta)dV^\beta + \sigma^\alpha dA^\alpha + \sigma^\beta dA^\beta + \gamma dA^{\alpha\beta} + d(\kappa L). \qquad (180)$$

For thermodynamic potential J_r, the equilibrium principle is formulated as follows:

$$(dJ_r)_{T,p^\alpha,E,N_j,\mu_i} = 0, \qquad (181)$$

where N_j is the number of molecules of the immobile component j in the solid. The written expressions are sufficient to find the ultimate strength of a given body.

The further algorithm of actions is the following. It is necessary to completely define the function and explore it to the maximum using condition expressed in Eq. (181). The presence of a maximum means an unstable equilibrium, i.e. destruction of a solid body. This is where the strength limit comes from.

We present a summary of the final results [139]. For the case of capillary condensation (when the liquid is in the crack nose, as shown in Fig. 17)

$$E_t = \left\{ \frac{\sigma^\alpha \cos\phi}{bc} + \frac{1}{2bc}\left[\frac{\gamma r}{z_0}(\cos^2\theta + \sin^2\phi) - (\sigma^\alpha - \sigma^\beta)\frac{2r}{z_0}\cos\theta + \frac{d\kappa}{dc} \right] \right\}^{1/2}, \tag{182}$$

for the case of capillary evaporation (when the crack tip is empty and the curvature of the meniscus is of the opposite sign)

$$E_t = \left\{ \frac{\sigma^\alpha \cos\phi}{bc} + \frac{1}{2bc}\left[\frac{\gamma r}{z_0}(\cos^2\theta + \sin^2\phi) + (\sigma^\alpha - \sigma^\beta)\frac{2r}{z_0}\cos\theta + \frac{d\kappa}{dc} \right] \right\}^{1/2}, \tag{183}$$

and the common relation for both cases with using the Young equation

$$E_t = \left\{ \frac{\sigma^\alpha \cos\phi}{bc} + \frac{1}{2bc}\left[\frac{\gamma r}{z_0}(\sin^2\phi - \cos^2\theta) + \frac{d\kappa}{dc} \right] \right\}^{1/2}. \tag{184}$$

where ϕ is half of the frontal angle, and z_0 is half of the crack mouth width (Fig. 17). Beyond the scope of the Young equation, Eqs. (182) and (183) can also be combined by the common notation

$$E_t = \left\{ \frac{\sigma^\alpha \cos\phi}{bc} + \frac{1}{2bc}\left[\frac{\gamma r}{z_0}(1 + \sin^2\phi) - (\sigma^\alpha - \sigma^\beta)\frac{2r}{z_0} + \frac{d\kappa}{dc} \right] \right\}^{1/2}. \tag{185}$$

In the expressions obtained, the first term is the main one, and the correction terms are combined in square brackets (taking into account the coefficient in front of them).

8.9. Final Remarks

When [127] was published, the reviewers asked: why such a strange name, "*J*-potential?" Historically, the names of thermodynamic potentials were often associated with energy, the ancestor of all potentials (free energy, bound energy, although the latter as a potential was never put into practice) or with the names of the authors of the introduced potentials (for example, free energies of Helmholtz and Gibbs). However, the frequent use of the term requires its brevity, and now only the name of Gibbs in the term "Gibbs energy" has survived from the names [125]. Gibbs himself, although he used several thermodynamic potentials, did not name them in any way (except for energy). He denoted them in Greek letters and later said: "the function is such and such." When switching to the Latin alphabet, it turned out that most of the designations of thermodynamic potentials (*E*, *F*, *G*, *H*) are adjacent to the letter *E* of the Latin alphabet, which is often used to denote energy. It is logical to supplement this sequence with the letter *I*, but it is actively used in physics for other purposes. And then comes the letter *J*, and it fits perfectly. Of course, it was tempting to somehow connect the desired letter with the author's surname, but the letter *R* in thermodynamics is securely assigned to the gas constant. So, *J*-potential, and in the Gibbs style, the name of the thermodynamic potential simply coincides with its designation. By the way, there are already similar examples in science. For example, in electrokinetic phenomena, one of the electric potentials is simply called the ζ-potential.

Unfortunately, *J*-potential did not manage to get into the textbook [125], and so far only one person has used it, the author himself. Several areas of application have been demonstrated by his efforts. As early as [127], it was shown how easy it is to derive the classical Neumann and Gibbs equations, including the Young equation, using *J*-potential (we did this above using the more practical hybrid *J*-potential). It should be noted that in principle all thermodynamic potentials are similar. The whole question is the convenience of their use and the conditions when they work. Let us hope that nanoscience "finds" its native thermodynamic potential and finds harmony with it. But this will take time.

9. CONCLUSIONS

After finishing, I hope, not a very tiring review of the works that we qualify as discoveries, the reader may have a question: how did all this affect the author and what was he ultimately rewarded with? One can look at scientific success in different ways, and, approaching the 90-year milestone, I cannot but remember that in science I came from the 50s and 60s. The Iron Curtain completely ruled out brain drain, and when I entered the Faculty of Physics at Leningrad State University in 1949, I found myself surrounded by the most able and talented people. This applied to both teachers and students. Some of them became my lifelong friends, later turning into remarkable scientists (two academicians left my group). And the undergraduates immediately shocked me: they stayed at the faculty in the evening to hear again the lecture (usually the most difficult one) given in the afternoon from the lips of one of their "geniuses" with his comments. Is this not a genuine and deep interest in science? And its educational value is obvious.

I remember that already in our time we buried my friend Professor V.V. Krotov (once recognized as the best scientist of the Faculty of Chemistry of St. Petersburg State University), and his daughter Irina, who came from abroad, gave us a dressing down: "What are you portraying here for world sorrow? Need to rejoice. The man lived a wonderful life. He always did what he wanted!" The last phrase is key. Far from every person, and even a scientist, one can say so. But you can also talk about me. And to the mercantile question "What does it give?" it is necessary, first of all, to answer that scientific activity is not a job, but a way of life. It is a game of the mind and the search for a solution (sometimes even in a dream) of one puzzle after another. It becomes especially gamble when several people participate in it. And, since the discovery of new phenomena is always a collective matter, I would like to sincerely thank the co-authors of all the phenomena described in this review. Some of the co-authors passed away, leaving in my heart eternal sympathy and indelible memory. Others are still alive, and I sincerely wish them new success!

Behind shoulders, there is a long way. There were ups and downs, awards and gold medals, but all this does not change the essence of the matter. For a scientist, scientific achievements themselves are a reward. They bring joy, make the scientist happy. And if there is someone else that needs to be remembered and thanked, it is fate that assigned me such a wonderful field as science.

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CONFLICT OF INTEREST

As noted in the review, a conflict of interest arose in 1976, but was removed by the publication [57]. There is currently no conflict of interest.

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