«Hidden» thermodynamics – rational approach to known facts

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1. The discrepancy between the approaches to the second law of thermodynamics and phase equilibrium. Solid and liquid solutions, *Issue 109, December 2015, 17-23.*
2. Entropy effects in real systems,. *Issue 110, January 2016, 14-19.*
3. Entropy effects in multiphase systems. Phase diagrams and eutectics melting mechanism, *Issue 111, February 2016, 28-33.*

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Introduction to all 3 parts

Almost all natural processes are described by the laws of thermodynamics – the first (the law of energy conservation) or the second, determining the direction of physical-chemical processes. The first law of thermodynamics is pretty clear, but it is not properly understood all the time. Sometimes the fact that there are no ideal isolated systems is ignored. Sometimes the energy disappears when in the description of wave annihilation in a counterphase. Many physics textbook note – in interference and diffraction, waves, if shifted by 180 degrees, damp each other and energy disappears. I have mentioned this in an article [1]. As an additional example, fig.1 depicts wave interference pattern generated by the source when reflected. According to a common physics approach, there are no oscillations to the right from the source in a narrow strip, and, therefore, energy. And it is not correct as energy can't disappear, it only transforms from one form (state) to another (currently unknown).

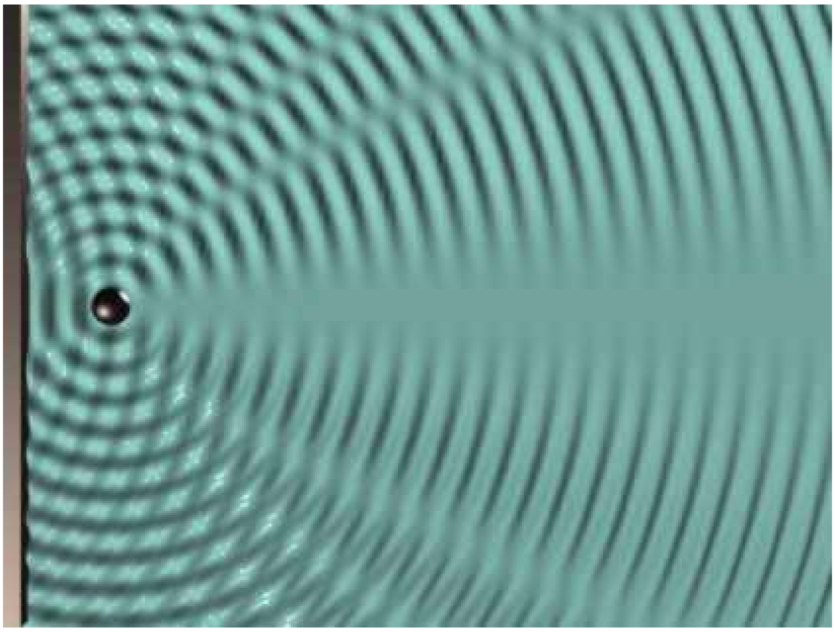


Fig. 1. Wave interference pattern during the reflection from the wall

As for the second law of thermodynamics its interpretation is more difficult, because its physical meaning, especially in regards to free energy and mixing entropy (statistical entropy) is badly understand and rarely approached to understand. This does not prevent us from using this law and related formulas to describe physical-chemical processes. Just as we use the other occurrences – gravity, quantum mechanics, nuclear structure etc. We only need to properly use the mathematical formulas and get the result.

But should we try to understand the physical meaning laws, if we've already learned to use them? Of course, it is a rhetorical question, just as the question of the necessity of the progress itself.

Nothing is perfect even from the scientific point of view. Judging by the fact, that the formulas failed to give us antigravity, quantum movement or proper cold nuclear synthesis, it is made clear that the mathematical physics are very limited. We resemble apes, barely capable of operating simple machines.

But let's get back to thermodynamics. Why do we need to know the physical meaning of its laws and what helpful information can we get?

I have tried to show what new discoveries are hidden by the simple formulas of the second law of thermodynamics and what is their practical use (see the second part of the article). As an example, the energy context of mixing entropy is revealed as well as the cause of the high strength of so called High Entropy Alloys (HEA) or (Superalloys). Came closer to create a corrosive-resistant iron (non-rusting iron), akin to the Delphi column in Deli. Shown, that the energy of mixing entropy also acts in heterogenic alloys, where there are no «pure» mixing effects. Reveal its influence on the properties of multiphase alloys; explain the melting mechanism of eutectics and the "depressed melting" process etc. Show the possible usage of thermal oscillation energy of molecule mixing. A particular case is the description of the phase equilibrium and phase diagrams in regards to the energy of the configurational entropy.

Due to a large amount of material, the article is separated into three parts [2-4].

General contents are provided as followed.

Content

Part 1.

The discrepancy between the approaches to the second law of thermodynamics and phase equilibrium. Solid and liquid solutions

It is obvious, that there should be a direct connection between the thermodynamic and physical properties of the matter. At present it is tried to connect the matter stability with exothermic reactions, occurring in the formation of alloys or chemical compounds. But the mixing entropy gets ignored during this, because, according to accepted theories, it is not related to energy and is just a measure of disorder [5].

Should be noted that the classics of thermodynamics, such as Gibbs, Cahn, Swalin, Yum-Rosery, Neyman-Kopp and others in their earlier works have tried to rethink the physical meaning of many abstract statements of thermodynamics, particularly the entropy [6-8]. It is not coincidental that in choosing the very term "entropy" (transformed energy) Clausius underlines the following: "I have deliberately chosen the word entropy to be as similar as possible to the word energy: the two quantities to be named by these words are so closely related in physical significance that a certain similarity in their names appears to be appropriate." [6]. But their attempts to fill the main principles of thermodynamics with physical meaning have not been put into the system, and, sadly, are forgotten.

At present there is no agreed upon definition of "entropy". There is one approach to entropy and free energy in the alloys thermodynamics, another in chemical thermodynamics, third in mechanics and heat processes, etc. If we add many unconnected modifications of entropy, for example, informational entropy, entropy of stars, Big Bang and Universe expansion entropy, etc, there comes a misunderstanding. It is a tradition to connect any new occurrence with entropy to make it sound more scientific. At the same time entropy should have specific physical meaning closely connected with energy.

In our opinion, even during the ideal mixing (in the absence of visible release or absorption of heat), there are hidden self-compensating energy processes inside system, that occur in the physical-chemical processes [9-12]. There are energy emission due to the strengthening of interatomic bonds and its simultaneous absorption (completed work) due to the increase in the oscillatory energy, i.e. increase of the average heat capacity, which formula $\hat{\boldsymbol{C}} = \Delta \boldsymbol{Q}/\boldsymbol{T} = \boldsymbol{S}$ is equal to the oscillatory entropy formula. In other words the statistical entropy is also the oscillatory energy, which is proven, in particular by osmotic processes, where the mixing entropy executes work – creates the osmotic pressure.

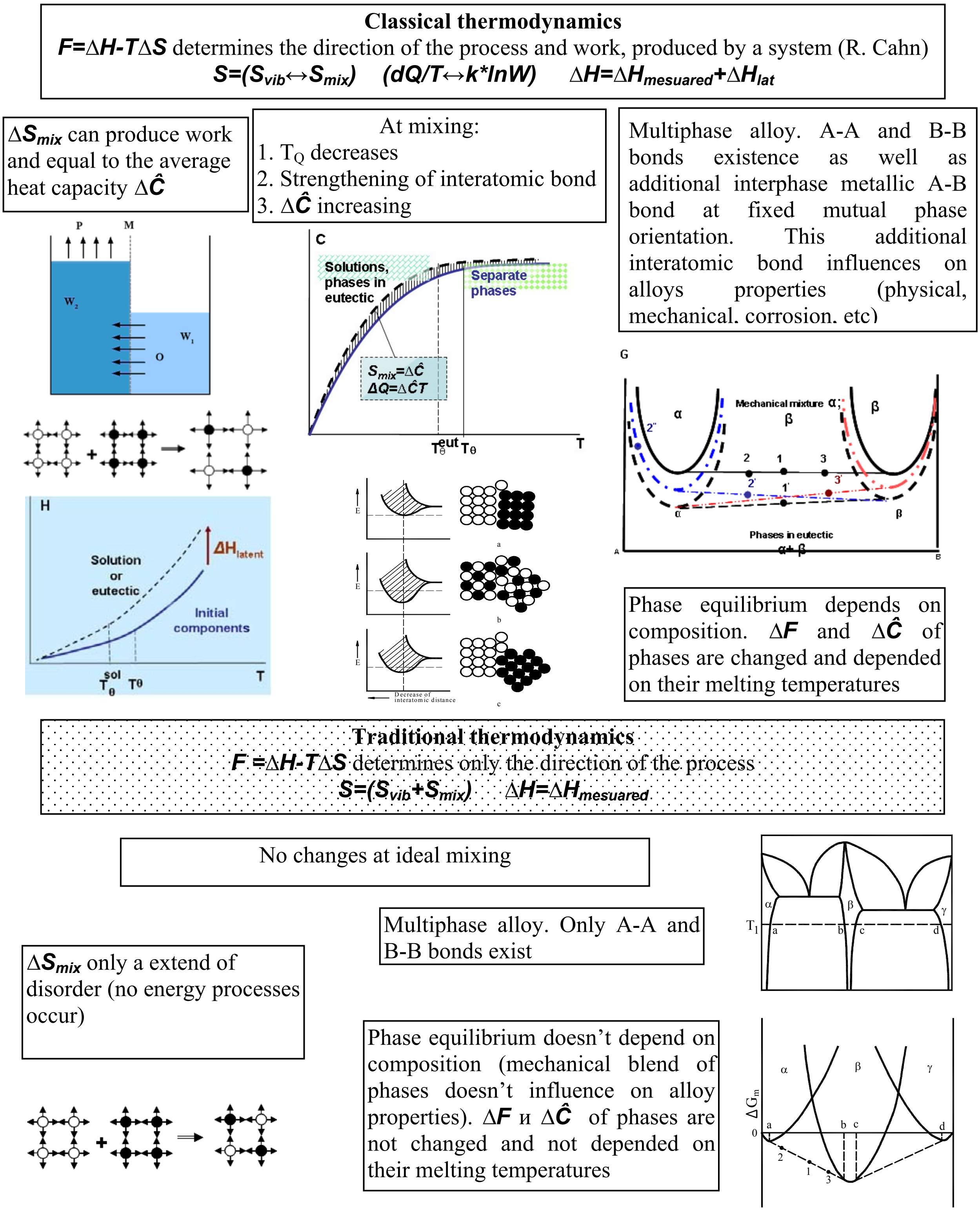
The need to view entropy as something beyond the abstract definition, developed to describe the Carnot cycle and the second law of thermodynamics, as something with a real physical meaning, confirms the newly discovered class of materials – so called High Entropy Alloys (HEA) or Superalloys [13-17]. They are the subject of several international conferences. They are multicomponent solid solutions on the basis of several systems, particularly iron and nickel – Fe-Ni-Al-Cr-Mo-Mn - etc.*, in which the value of mixing (configurational) entropy due to more than five components in the alloy composition is very high*. These alloys have stronger mechanical properties and high-temperature strength. This effect still unexplained.

Such alloys could be also formed in actinide systems with the wide region of mutual dissolvability of the elements, for example U-Th-Pu-Am-Np and the dissolve elements Zr-Mo-Nb-Ti etc. Based on these systems, it is possible to form high-entropy alloys with extraordinary high value properties. This alloying approach could be applied to many other systems.

The discrepancy of classical and traditional approaches to the thermodynamics of alloys also exists in the heterogeneous systems – multiphase alloys. It is especially visible in eutectic alloys, where the real state of an alloy as a unified thermodynamic system contradicts currently existing the thermodynamic description of an alloy as a mechanical mixture of phases. A.A. Bochvar, in particular, in his studies of eutectic alloy crystallization, pointed out the fact of an intricate physical and chemical interaction between phases, that does not take place in a mechanical blend. It points out that the melting temperature of alloys always differentiates from the melting temperature of a mechanical blend: "Eutectics cannot be called a mechanical blend of phases, which is sometimes done. There is no interaction between phases in a mechanical blend. On the contrary, a complicated physical and chemical interaction between phases is observable in the eutectics" [18].

However the traditional thermodynamics of alloys, when used to describe the phase equilibrium of complex systems with geometric thermodynamics method, *retains the mechanical approach to alloys, even eutectic* by separating the system to isolated components, then united by a mechanical mix principle [6, 19-23]. Thus, it ceases to respect the equilibrium principle and the striving to the minimum free energy, contradicting the classical thermodynamics – that described any complex system as a united thermodynamic system. ***As a result, a whole series of phenomena that affects both the properties of alloys and the processes of crystallization and structure formation of alloys get ignored.***

For example, in the traditional description of the phase equilibrium with the second law of thermodynamics, the energy value (meaning) of configurational entropy and, hence, free energy gets ignored, as does the fact, that the second law is formulated from the first law, the law of energy conservation and, therefore, is related to energy. This is, most of all, applies to the energy of atomic oscillations and the strength of interatomic bond, not shown in the mathematical description of Gibbs's balance. Moreover, in the free energy equation (the second law of thermodynamics) *the energy contribution* of the second term is not taken into an account. This concerns entropy, most of all mixing entropy during formation of alloys, solutions and other physical-chemical processes, because it is agreed upon that the mixing entropy cannot produce work (energy). This and the other contradictions between the traditional and classic thermodynamics are provided in a scheme (fig. 2).



Classical thermodynamics

$F = \Delta H - T\Delta S$ determines the direction of the process and work, produced by a system (R. Cahn)

$S = (S_{vib} \leftrightarrow S_{mix})$ $(dQ/T \leftrightarrow k*\ln W)$ $\Delta H = \Delta H_{mesuared} + \Delta H_{lat}$

ΔS_{mix} can produce work and equal to the average heat capacity $\Delta\hat{C}$

At mixing:

1. T_Q decreases
2. Strengthening of interatomic bond
3. $\Delta\hat{C}$ increasing

Multiphase alloy. A-A and B-B bonds existence as well as additional interphase metallic A-B bond at fixed mutual phase orientation. This additional interatomic bond influences on alloys properties (physical, mechanical. corrosion. etc)

Phase equilibrium depends on composition. ΔF and $\Delta\hat{C}$ of phases are changed and depended on their melting temperatures

Traditional thermodynamics

$F = \Delta H - T\Delta S$ determines only the direction of the process

$S = (S_{vib} + S_{mix})$ $\Delta H = \Delta H_{mesuared}$

No changes at ideal mixing

Multiphase alloy. Only A-A and B-B bonds exist

ΔS_{mix} only a extend of disorder (no energy processes occur)

Phase equilibrium doesn't depend on composition (mechanical blend of phases doesn't influence on alloy properties). ΔF и $\Delta\hat{C}$ of phases are not changed and not depended on their melting temperatures

Fig. 2. Illustration scheme of contradictions between the traditional and classic thermodynamics [7-8]

Study goals:

Expand the interpretation of main thermodynamic principles, based on the less-known theories of the classics in the field – Gibbs, Cahn, Swalin, Neyman-Kopp and others.

Try to understand the physical meaning of such abstract concepts as configurational entropy and free energy, their energy context.

Show that heat emission, heat absorption and the increase of average heat capacity occur even during the ideal mixing, when A-A and A-B bonds are considered indistinguishable.

Reveal the latent processes that occur in the mixing and phase transformations, causing the change in the character of atomic oscillations, increasing the average heat capacity and strengthening interatomic bonds.

Show the possible uses of the new approaches in the development of novel materials and High-entropy alloys, description of the plutonium delta phase as well as the increase of corrosion resistance in non-alloyed iron (non-rusting iron) by increasing configurational entropy in electron states.

Determine the particularities of thermodynamic laws usage when applied to the complex multiphase alloys, contradiction in the description of state (phase) diagrams by the geometric thermodynamics.

Determine the influence of the additional interphase metallic bond on the physical-mechanical alloy properties.

Clarify the mechanism of eutectics melting and the "depressed melting" process.

Etc

Conclusion *of all three articles*

1. Statistical (mixing) entropy is identical to the vibration entropy, has an energy context, expressed through the change in the nature of atomic oscillations, can be expressed also as **dQ/dT,** which is proven, in particular, by osmotic processes.
2. In Cahn's interpretation of the second law of thermodynamics Helmholtz free energy is defined as a work, or amount of energy taken with opposite sign, that could be potentially performed or dissipated by the system. The main contribution to the free energy value change is made by the entropy part of equation **TS**, hence, entropy of mixing that has an energy meaning.
3. Mixing process are hard to observe because they occur inside the system and are accompanied by the increase of average heat capacity due to the decrease of Debye temperature, which, according to Lindemann's rule, lowers down the melting temperature;
4. Even in an ideal mixing, two hidden (latent) processes go on at the same time and compensate each other. First - the increase of average heat capacity, requiring heat absorption to support the constant temperature. Second - at the same time, latent (hidden) heat emission (release), $\mathbf{Q} = \Delta\hat{\mathbf{C}}\mathbf{T}$, or hidden enthalpy increase, through the strengthening of interatomic bonds that is confirmed particularly in **HEA.**
5. The second law of thermodynamics can be considered as a law of energy conservation, because it reveals the hidden energy processes, occurring inside the system.
6. Practical use of novel approaches to alloys theory and thermodynamics based on hidden effects at mixing processes and energy sense of configurational entropy is considered.
7. Explanation is given to unique properties of so-called high-entropyalloys (HEA) by additional strengthening of interatomic bonds in mixing (formation of liquid and solid solutions). Ways of improving its properties is shown.
8. New approaches to modify the thermodynamic databases and programs, like CALPHAD (CALculation of PHAse Diagrams) and Thermo-Calc, by including additional thermodynamic data and formulas, such as the energy of configurational entropy, average hear capacity of phases in isolated state and in contact, the change in Debye temperature during alloy formation, etc is proposed.
9. With the use of energy sense of configurational entropy an attempt is made to explanation of anomalous in actinide systems behavior, particularly plutonium, as configurational entropy changes during heating and microalloying. It is based on two main principals:

9.1. Plutonium should be considered not as a separate element, but as a multicomponent alloy, with plutonium serving as separate components in various electron and phonon states. As a result, the contribution of mixing entropy to the phase properties, stability and transformations increases.

9.2. Unlike common alloys, entropy factor (mixing entropy) changes along with the temperature and the correlating Debye temperature, causing the delta phase crystal lattice compression at heating and other unexpected properties of Pu.

10. An attempt is made to find out the secret of the Qutb column in Delhi made of non-rusting iron. Increasing the mixing entropy of valent electron states by complex electromagnetic and thermal treatment we preliminary received the similar corrosion resistant parameters on nails.

11. Carefully studied the mechanism of osmotic pressure formation based on energy substance of configurational (mixing) entropy. It is shown that if we separate in time the energy release and increase of average heat capacity during mixing processes, heat pump based on the osmotic pressure – "perpetual mobile" of the second type can be created without violating the second law of thermodynamics.

12. Reverse transformation of vibrational entropy into configurational one is considered taken into account the increase of a number of molecules states with various speeds and energies, particularly with the increase in temperature as pseudo-mixing process.

13. Consideration is given to the possibility of molecules heat energy use. It is found the additional limitation to this process in addition to the limitations of the second law of thermodynamics.

14. Shown that at crystallization, where the homogenous mixture separates into heterogeneous solid phases, the energy content of mixing entropy does not disappear but transforms into vibration entropy. This effect, just like in solid solutions, causes an increase of the average heat capacity and simultaneous strengthening of interatomic bond energy.

15. As a result a mismatch is discovered between the thermodynamic description of alloys as a mechanical phase mixture and their actual state as a unified thermodynamic system, where an intricate physical and chemical interaction between phases is observable. Hence, for describing the thermodynamic state of alloys it is suggested in place of the presently adopted values of isolated phase free energies to use the free energies of the same phases contacting one other. As a result the free energy of an alloy is reduced.

16. Therefore, the average heat capacity values of the phases comprising a multiphase alloy or eutectics become higher than in the original isolated phases. Hence, considering thermodynamic phase equilibrium and following Gibbs interpretation, dependence of the free energy values of mixed separate isolated phases versus composition shall be not-linear as it is presently assumed but a parabolic one as for solid and liquid solutions.

17. This bond between phases akin to a metallic bond, *where valent electrons of one phase interact with the valent electrons of another eutectic phase through mutually oriented interphase borders. As a result, the atomic fluctuation nature changes, the Debye temperature lowers, causing the melting temperature to lower as well. As a result, the free energy value of the system decreases.*

18. Phases in eutectics additionally forms internal bonds that distinguish alloy from a mechanical blend of phases. This bond can arbitrarily be called an interphase metallic one. The interphase metallic bond in alloys at the interatomic level shows up in the fact that despite the existence of individual phases A and B and internal bonds A-A and B-B in the structures of alloys these phases partially also retain the A-B bond that is only characteristic of a liquid state. This bond reveals as the partial splitting of the electron levels that corresponds to the A-B state and exists until the specific mutual phase orientation is retained. Therefore valent electrons of one phase can interact with the valent electrons of another eutectic phase though mutually oriented interphase borders. As a result, the atomic oscillations nature changes, the Debye temperature for eutectic alloys becomes lower that make them melts at lower temperatures simultaneously in the whole alloy.

19. Preliminary tests on various aluminum eutectic alloys proved this hypothesis. By changing the mutual orientation of phases we managed to overheat the alloy by 22 degrees Celsius over the melting temperature without a phase change at a low heating speed (80 degrees/min).

20. The interphase metallic bond is one of the previously unknown varieties of interatomic bonds that exists between phases both in solid and solid-liquid states, that is why, it influences many properties of alloys. As forming alloy (particularly eutectic one) we observe changes in free energy, entropy, heat capacity and hence – in character and energy of atomic oscillations. Therefore it affects: temperature and enthalpy of melting, heat capacity, coefficient of thermal expansion, strength and high temperature strength as well as diffusion processes, that in turn influences on compatibility, corrosion, material performance, etc

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1. Introduction

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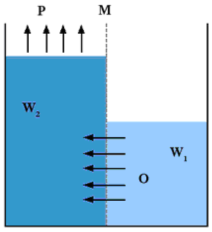
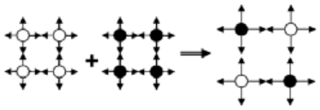
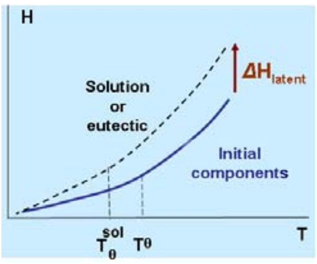
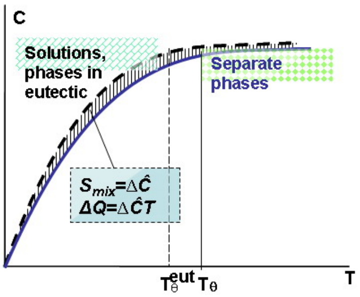
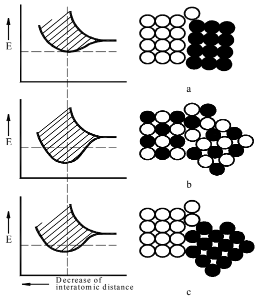
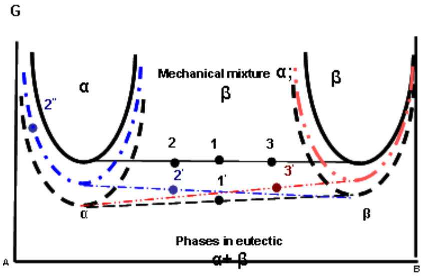












Phase equilibrium depends on composition. ΔF and $\Delta\hat{C}$ of phases are changed and depended on their melting temperatures

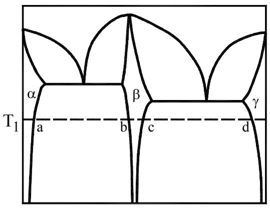
Traditional thermodynamics

$F=\Delta H-T\Delta S$ determines only the direction of the process

$S=(S_{vib}+S_{mix})$ $\Delta H=\Delta H_{mesuared}$

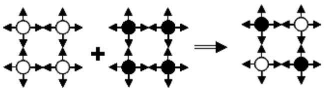
No changes at ideal mixing

Multiphase alloy. Only A-A and B-B bonds exist



ΔS_{mix} only a extend of disorder (no energy processes occur)

Phase equilibrium doesn't depend on composition (mechanical blend of phases doesn't influence on alloy properties). ΔF и $\Delta\hat{C}$ of phases are not changed and not depended on their melting temperatures



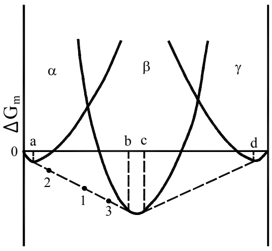


Fig. 1. Illustration scheme of contradictions between the traditional and classic thermodynamics [7-8]

2. The connection between the first and the second law of thermodynamics

In order to understand the hidden processes occurring in physical chemical interactions, the formation of alloys and solutions, we should return to the main laws of thermodynamics, try to understand their physical meaning and their mutual connection.

The First law is formulated as the law of energy conservation. Energy of the system can be increased by doing work on it or sending it an amount of heat. Energy of the system decreases, when the work is being done by the system itself, or when the heat is taken from the system.

Therefore, the First law of thermodynamics for a system of constant mass may be represented by the equation [3, 4]:

$$\Delta U = Q - W \quad (1),$$

Where **ΔU** – change of the internal system energy in a given process, **Q** – heat volume that the system got from the environment and **W** - work, done by the system on the surroundings.

Traditional graphic presentation first law of thermodynamics is provided in fig. 2 [3].

Obviously, if the system absorbs heat from the environment, its internal energy increases (positive **Q** value). Most frequently it occurs when the **temperature of the environment is higher, i.e. there originally was a difference in temperature.** Internal energy of the system may be reduced, if the system does work over the environment, or when there is heat (energy) being taken out of the system. This case is shown on fig.2 (c). This scheme illustrates the *reversible* processes.

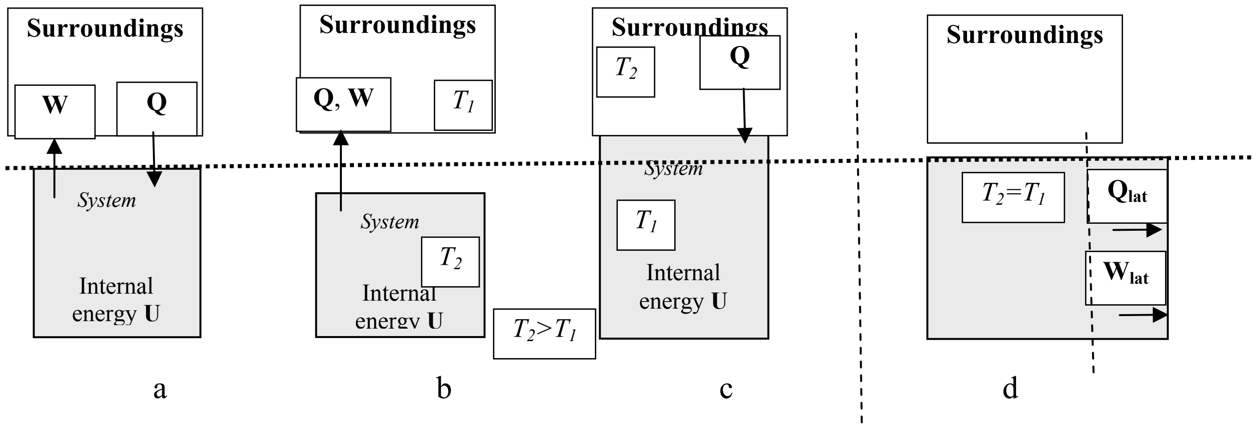


Fig.2. Graphic presentation of the first law of thermodynamics, a – traditional view [4], b – system released energy or done a work, c – system absorbed energy, d – proposed approach - increase of internal energy due to the increase of heat capacity (by mixing of components) - system has done work itself to increase internal enthalpy - average heat capacity, and simultaneously has filled it with the heat energy. With that the value of internal energy has increased [6-8].

Let's try to apply this scheme and take a look on a hypothetical case, where there is work done on the system, but it is done inside the system and by the system itself – common for spontaneous chemical reactions (irreversible processes). Obviously, the internal energy should be increased, because the work remained inside the system, as illustrated in (fig. 2 d) [6-8]. Further, we are going to show, that this type is realized in ideal mixing.

One of the universal principles of the nature is - *any system seeks the minimum of energy to achieve the most stable condition.* For example, the electrons seek to fill the lower energetic levels in atoms, or the creation of more stable chemical compounds occurs. In all of these processes the heat emission occurs (fig. 2b), the internal energy decreases and the system achieves the more stable state (condition).

But some processes, for example, spontaneous mixing, can occur even when the internal energy of the system **(ΔU)** *increases and there is no temperature difference between the system and the* environment. This mostly occurs in the irreversible processes, where the second law of thermodynamics should be used. *But the first law must be respected too.*

For example, a spontaneous dissolution of glycerin in the water causes the solution to cool down. After that, there is a spontaneous increase of internal energy due to taking energy from the environment, **i.e. the system must do work.**

From the first sight, this process contradicts the first laws – i.e. the law of energy conservation – no work done by the system or done on the system is observed, but the internal energy increases (the system itself takes heat out of the environment).

So, if the system cooled down after mixing, it means that the energy was taken from it – like in a heat pump scheme, there was work done on the system. But we can't see it, even while the First law of thermodynamics **requires to find it.** Thus, we can propose, that the **work was done inside the system** and it caused the system cooling down.

Because the work remained inside, the enthalpy **(ΔH),** equal to the internal energy **(ΔU)** under constant pressure, increases, and, therefore, the internal energy increases too. Further we will show that the law of energy conservation is also respected in spontaneous processes and that the increase of internal energy occurs not due to the environment, but due to the internal system processes (hidden or latent work and hidden release of energy $\mathbf{W_{latent}}$ or $\mathbf{Q_{latent}}$ fig. 2d). But this property is ignored by traditional thermodynamics, thereby ignoring the law of energy conservation.

However, could such processes be described by the first law of thermodynamics? Yes, if we understand the energy context of the irreversible processes described by the second law of thermodynamics and compare them to the first law. A distinct feature of the irreversible processes is the fact that they mostly occur inside the system, and are, therefore, latent. In this case, the system acts both as a system and as an surroundings [6, 7, 21]. Thus, the common interpretation of the energy conservation law is very general, consider only interaction of system with the surroundings and does not reflect on the internal processes, occurring in the system.

First of all, those are irreversible processes, occurring, for example, during mixing – chemical reactions, formation of solutions and alloys, etc.

If we again return back to the process of glycerin dissolving in the water, from the first sight it contradicts the law of energy conservation – there is no work done by or on the system, but the internal energy increases (system itself takes heat from the surroundings).

Even stranger is the ideal mixing process – when the mutual diffusion process occurs without visibile energy effects, while no system parameters and the internal energy seem to change. Traditional description of this process is schematically presented on fig. 3a [6, 7, 21].

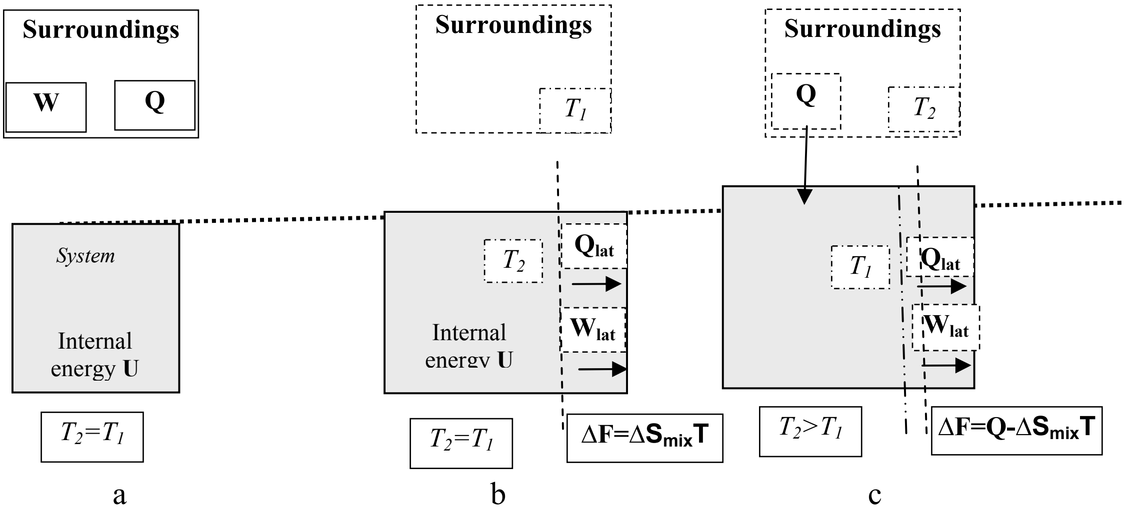


Fig.3. Graphic presentation the second law of thermodynamics:

a – ideal mixing (traditional view, violates The First law of thermodynamics), b – ideal mixing not violating the first law of thermodynamics (proposed variant) [6, 7, 21], c – mixing with the absorption of the energy (positive energy of mixing).

*Increase in the internal energy occurred due to the internal system processes - increase of the heat capacity (mixing of components) – system had done work on itself to increase the heat capacity – and, at the same time, filled it with thermal energy. The internal energy value increased for the value Δ**F**.*

But this is not true. Even in the ideal mixing some work must be done and be reflected in the internal energy change. It is a non-equilibrium process – therefore, if we want the mixed atoms to separate, i.e. the system must be returned to the original state, *a work should be done*. In other words, there is a hidden work in a spontaneous mixing process that is not reflected in the traditional view on the second law of thermodynamics.

In order to explain such effects, traditional thermodynamics recommends us to ignore the law of energy conservation, and use the second law of thermodynamics. It is considered that the second law of thermodynamics only determines the direction of physical chemical processes and not the energy balance. As a result, a contradiction between two laws arises.

In our opinion, the visible discrepancy in laws happens, firstly, because of the insufficient understanding of the energy meaning of the second law. Secondly, at mixing hidden processes are unaccounted – they occur inside the system in the opposite energetic directions and compensating each other. Therefore, they don't interact with the surroundings, like in the first law and are not seen from the first look. For example, if the work is done inside the system itself **(W_{lat})** or the heat is release and, simultaneously, the heat capacity of the system increases, then we won't see any changes on a calorimeter, but the real enthalpy and internal energy would increase, and all related parameters would change – free energy, heat capacity, interatomic bond strength etc [6, 7, 21]. In this case we can **expand** the second law interpretation not only to determine the direction of physical chemical processes, but also to define the energy balance as well, like in the first law. This approach is presented in fig. 3b, c, is detailed further (fig. 16). In this interpretation, the mixing entropy influences the rise of internal energy as well.

3. Cahn's interpretation of the second law of thermodynamics

The first one to define the energy meaning of the second law of thermodynamics and its connection to the first law was Cahn in his book «Physical Metallurgy » (second edition).

Cahn's method was simple. Under constant pressure **P** and temperature **T**, where internal energy **ΔU is equal to enthalpy ΔH,** he included entropy **S** into the first law equation**,** expressing it by heat **Q, i.e.** $\Delta Q = T\Delta S$

Then, by a simple mathematical action on the first law **($\Delta U = Q - W$),** he got:

$$-W = \Delta U - Q = \Delta H - T\Delta S = \Delta F \quad (2)$$

where ΔF – new function of the system state, called *Helmholz's free energy.*

As a result, Cahn got a mathematical expression of the second law of thermodynamics from the first law. That resulted in following:

$$-W = \Delta F \quad (3)$$

This result has important meaning. As further Cahn writes: «free energy is the work, taken with the opposite sign that system could have potentially done at the constant temperature. So, factually, he directed to the energy meaning of the free energy and, therefore, entropy. With that, he did not separate entropy into vibrational and configurational (statistical), because he fairly thought that they represent the one state. But in the following editions editors have taken this paragraph out, judging it unnecessary and without interest.

Cahn's interpretation of the second law has foundational meaning, as it opens the way to understand the physical nature of the second law, free energy and entropy.

It should be noted that energy interpretation of the free energy as the useful work is also known in the thermo-chemistry (chemical thermodynamics) [20], but, as with Cahn's, this idea has not been developed further.

This mathematically flawless interpretation expands the interpretation of the second law from the direction of occurring processes and chemical reactions, to revealing its energy nature – as an **energy that can be turned into work.**

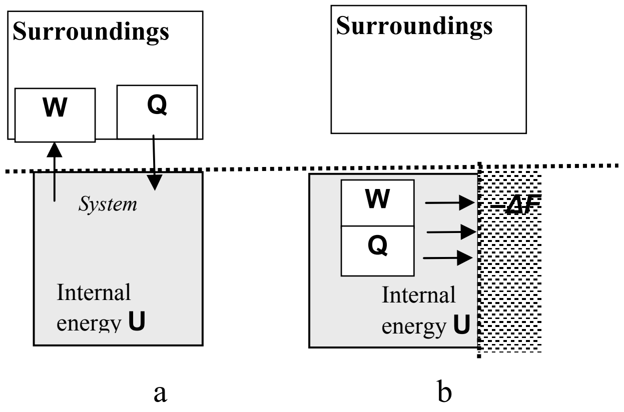


Fig. 4. Graphic presentation of the first (a) and the second (b) laws of thermodynamics: **($-W = \Delta F$)** *the system done work over itself to increase the heat capacity. With that the internal energy value increased.*

Therefore, we can include additional and irreversible work done to the scheme that caused internal energy to increase. This additional work is equal to $-\Delta \mathbf{F}$ and shown as a hatched area on the (fig. 4). As an example, work was done inside the system and did not go to the environment, but stayed inside the system and caused the internal energy to increase, like in the first law.

It should be noted that Cahn expanded the energy interpretation of free energy and entropy, applying it to all spontaneously occurring processes. He writes: «The conclusions are reasonable for any isolated system with spontaneous heat transfer. It may look like they are useless for metallurgy. But it is not true, since the increase of entropy occurs *in all* spontaneous processes in an isolated system. For example, gas expansion, diffusion in metals and chemical reactions cause an increase of isolated system entropy, when these processes occur spontaneously. Any natural processes occurring in an isolated system would cause the system entropy».

Further we would try to show the result of free energy and entropy transformation in spontaneous processes through the changes in oscillation energy and strengthening of interatomic bonds.

4. Energy nature of configurational entropy.

While studying configurational entropy or mixing entropy, we should remember that, despite its statistical nature, it is as vibrational entropy also a full entropy. Cottrell notes in «Structure of metals and alloys»: «*Formally, both entropies are thermodynamic measures of one system property and statistical entropy is identical to the formal vibrational entropy. Therefore the statistical factor acts as a numerical expression of energy relating to temperature, e.g. vibrational entropy.* » We are going to return to this definition many times later.

Let's try and expand this idea – try do determine the place of this potential work or energy of configurational entropy *in a thermodynamic* process? We are going to look at a standard mixing process that accompanies all chemical reactions and the alloy formation:

$$\Delta \mathbf{F} = \Delta \mathbf{H} - \mathbf{T}\Delta \mathbf{S} \quad (4)$$

This equation consists of an energy factor **ΔH** and entropy factor **TΔS**. Numerically, an energy factor is evaluated from the value of a heat effect Δ**H** (under constant pressure). Change in enthalpy can be experimentally determined by a calorimeter. Entropy factor determines the system shift to a state of higher disorder and dominates at higher temperatures. Does it also have an energy nature? Because Clausius defined entropy as a «transformed energy».

For a simple approach let's look at the process of *ideal mixture* formation, where enthalpy **ΔH** is equal to zero and the change of free energy is determined only by an entropy part of the equation:

$$\Delta \mathbf{F}_{\mathbf{mix}} = -\mathbf{T}\Delta \mathbf{S}_{\mathbf{mix}}. \quad (5)$$

With that, the entropy part is not represented by vibrational entropy, which energy meaning is more or less clear, but configurational entropy, that has a statistical, probable and somewhat virtual nature. In this case, according to the Cahn's definition, mixing entropy that replace the free energy in ideal mixing, can do work, and, therefore, have an energy nature and not just a statistical definition. There are several proofs of that.

Nikolay Kozyrev [22-25] used the mixing and dissolution processes, where only mixing entropy increased, as processes that increase the energy of the system, as was registered by corresponding sensors.

During the studies of interconnection between the Physical Vacuum and the matter, we registered the irreversible weight change during the dissolution of sugar in the water – it signified the internal change, the increase of internal energy (under reversible processes weight restores) [5, 21, 26, 27]. But the main experimental proof of the energy nature of mixing entropy and free energy is osmosis.

5. Osmotic pressure as the result of useful work by configuration entropy (mixing entropy)

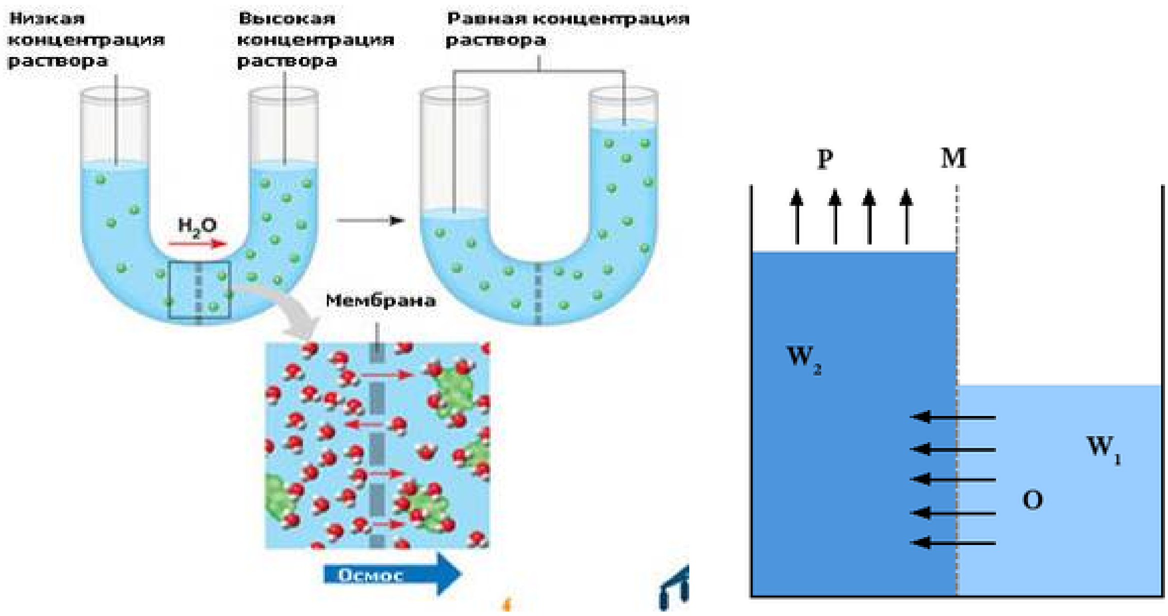
The main proof of the foundational statement made by Cahn – that the free energy and configurational entropy can do work – is the osmotic processes.

In each mixing a mutual diffusion occurs between the solvent particles and the particles of the diffusing substance. The moving force of the diffusion is the decrease of free energy of the system or the decrease of chemical potential of every diffusing component. If we only mix fresh and salt water, we can’t observe any hidden effects. But if we do this with the half-penetrating membrane, through which only solvent molecules can go through (half- penetrating membrane), an osmosis takes place (from Greek - push, pressure) - the process of one-sided diffusion of solvent molecules to the side of higher concentration of the diffused substance (lower concentration of solvent) through the half- penetrating membrane. The osmosis pressure occurs due to the striving of particles to equally distribute by the whole volume (fig. 5) [28]. Pressure strength is high enough, and can reach 20 atmospheres during the mix of seawater and fresh water.

The osmosis pressure value ***($P_{осм}$)*** is proportional to the solution concentration (***C)*** in mol-volume shares, and temperature ***(T)***, is determined by the Vant-Hoff equation:

$$\mathbf{P_{ОСМ}=RTC} \quad (6)$$

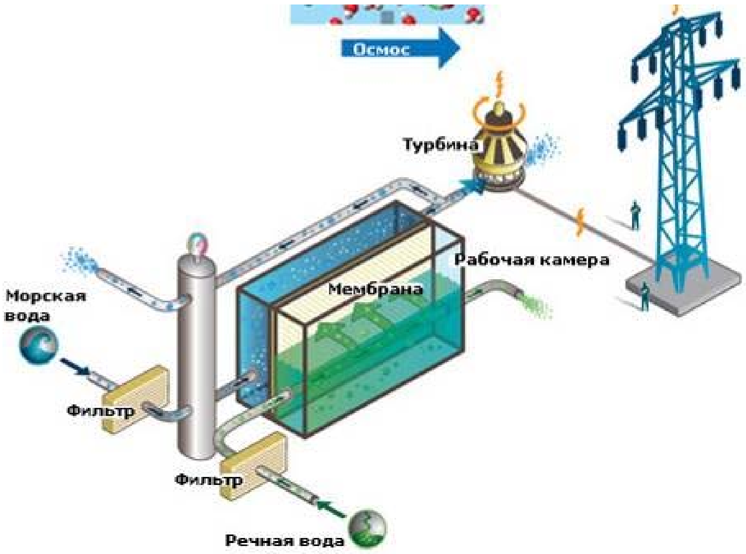
A wider interpretation of osmosis is based on the Le Chatelier-Brown principle: if a system in a balanced state is affected externally, by changing any condition of the balance (temperature, pressure, concentration, external electromagnetic field), inside the system the processes, directed to compensate external impact, become stronger. The striving of solvent molecules to penetrate the membrane is opposed by the increase in hydrostatic pressure (osmotic pressure). Its value is very high.



a b

*Fig. 5. Water transfer through a half-penetrating membrane - Solvent particles (blue) can penetrate the membrane, particles of the dissolved matter (red) — no (a)***,** *creation of osmotic pressure during mixing (b). W – concentration of the dissolved matter* ***(***$W_2 > W_1$***)***

Therefore, naturally, osmosis is applied in alternative power engineering. This process is currently used in the ***osmotic power plant in Norway.*** The first and only osmotic power plant is built in Norway town of Tofta by Statkraft company. Osmotic power plant controls the mixing of sea and fresh water, taking energy from the growing ***entropy*** of the liquids (fig. 6) [29]. The mixing occurs in a tank divided into two sections by a half-penetrating membrane. One section is filled by the sea water, the other one – by fresh water. Due to the difference of salt concentration in sea and fresh water, the water molecules from the fresh section, striving to balance the salt concentration, transfer through the membrane to the sea section. As a result of that process, an excessive pressure forms in the seawater section – which is used to rotate the electricity-generating turbine.



a

b

Fig. 6. Use of the mixing process in the osmotic power plant, basic structure of the plant (a), first osmotic power plant in the world (b)

The used process of simple mixing of fresh and salt water occurs almost without any heat effects and, at the first look, may be considered to be an ideal mixing. Therefore, in the mixing process through a half-penetrating membrane, all work is done by the free energy, just like in Cahn's work, - here, expressed by the ***mixing entropy.*** Therefore, *mixing entropy* can *do work and produce energy.* Further we are going to see, how it occurs and how the energy meaning of configurational entropy realizes itself. Naturally, we may presume that it is somehow connected with the heat capacity, i.e. energy and amplitude of interatomic oscillations, as it will be shown in chapters 6 and 7.

6. Interconnection of vibrational and configurational entropy

So, mixing entropy can produce energy and is connected with the energy of interatomic oscillations. But how is it realized? And, most of all, what is entropy and what is its physical meaning?

Most scientists think, that entropy is a united system property and should have a common physical meaning even when the artificial division in separate parts sometimes takes place. But in traditional thermodynamics, entropy is often separated and then not put back again. Therefore, the united physical meaning of the entropy process is lost.

For example, most often the entropy ΔS is divided into configurational (mixing or statistical) and vibrational:

$$\Delta S = \Delta S_{mix} + \Delta S_{vib} \quad (7)$$

This artificial division was best expressed by Hume-Rosary [5]: «For every alloy the complete entropy consists out of two terms.

The first one:

$$S = {}_0\int^T dQ/T = {}_0\int^T C_p dT/T \quad (8)$$

represents the change in entropy in the heating up from absolute zero to temperature T.

Second part of the solid solution entropy equation is called configurational entropy or mixing entropy:

$$S_{mix} = k \cdot \ln W, \quad (9)$$

where W - the number of distributions in the system, k - Boltzmann's constant

Therefore, the full alloy entropy equation is expressed this way:

$$S = {}_0\int^T dQ/T + k \cdot \ln W \quad (10)$$

Further he writes: «In solid solutions the first part is ignored».

Therefore, it turns out that at the constant temperature the vibrational entropy at mixing and at the formation of a solution does not change (remains in the original, pre-mixing state).

The simplified approach of traditional thermodynamics violates the classical definition of entropy as a common property of the system. As was shown with the osmotic processes, both entropies are connected with each other and mixing entropy can do useful work from atomic oscillations. Therefore, ignoring the vibrational energy in the description of a mixing process is a violation of the energy conservation law, i.e. the first law of thermodynamics. Dehlinger also confirmed it, underlining an internal connection of two entropies [30]: «The most important value in statistics is the thermodynamic probability of macro-state, which is a number of separate microstates. In the thermodynamic system, this value is a grade of splitting for electron states at the current energy value». As it is known, the degeneration causes a system energy decrease and, as a result, energy release. Further: «This value, called entropy, is an additive function of a macro-state and can be defined by a calorimeter». So, mixing entropy can be defined energetically, via the atomic oscillations, therefore, entropy is a united property of the system.

The classical approach to entropy was best expressed by Cottrell in his book "Structure of metals and alloys". He writes: "The internal energy does not define the equilibrium state of the system by itself. Another characteristic of the system defining the equilibrium is entropy. In thermodynamics entropy of the system is determined in abstract way. It is expected, that the system of absolute temperature **T** absorbs the infinitely small value of heat, not undergoing any other changes. That way, the entropy increases for the value **dS=dQ/T**"

Let's cite Cottrell further: "There is another interpretation of entropy, taken from statistical mechanics, allowing to compile the physical representation of entropy" ... "Statistical factor allows for disorder, connected to atoms oscillations in the crystal, and atoms arrangement disorder, appearing by melting the crystal or liquid evaporation." The measure for system disorder is **W** - the number of distributions, belonging to the system.

Numerically, the disorder is valued by a formula (9).

Then Cottrell writes: "Formally, both entropies are thermodynamic measures of one system property and statistical entropy is identical to the formal (vibrational) entropy. Therefore the statistical factor acts as a numerical expression of energy relating to temperature, e.g. vibrational entropy."

In out opinion, this conclusion is fundamental to understand the physical nature of entropy. Schematically this approach is represented in fig.7.

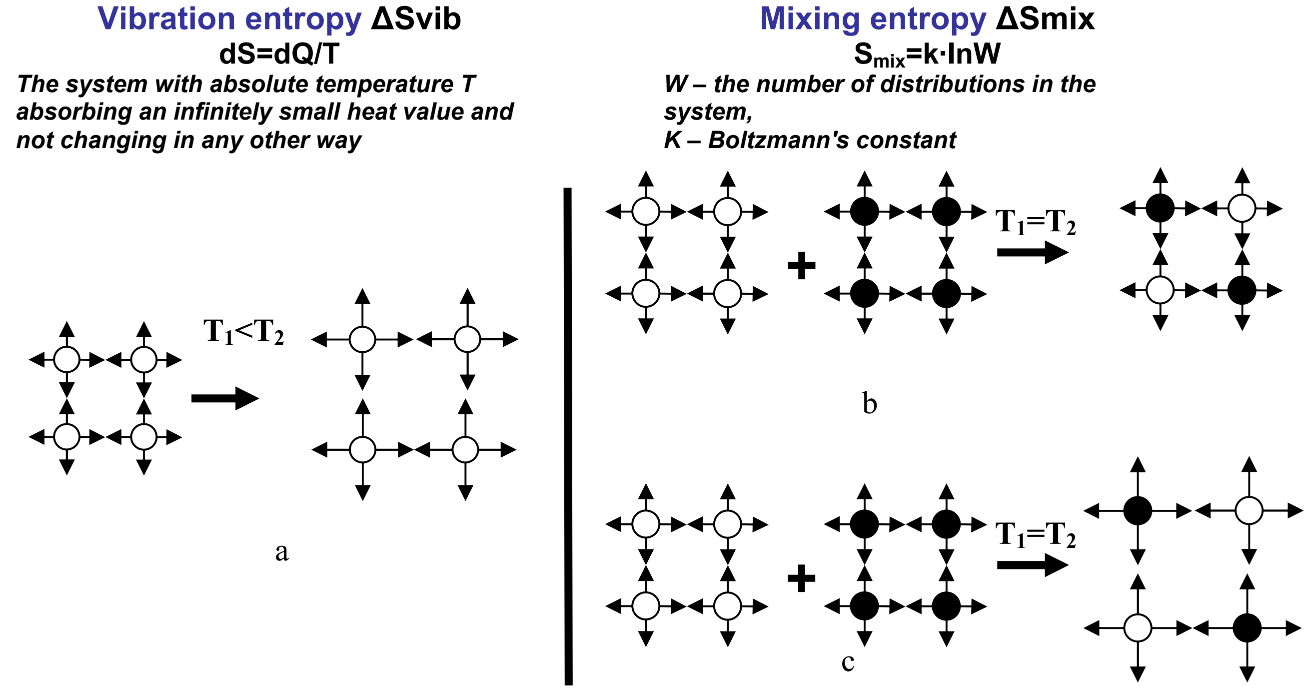


Fig. 7. Scheme illustrating the change in entropy: at heating - vibrational entropy (a), at mixing: b - traditional approach (no energy effects at the ideal mixing), c - classical approach (Cottrell) - mixing entropy transforms into the increase of vibrational entropy – our approach [6, 7]

Further, Cottrell attempted to answer the main question of the connection between mixing entropy and the energy and, therefore with vibrational entropy. “Why so? How the effect defined solely by the number of distributions is connected to energy? In can be answered by the following statements:

1. Various distributions of the system have various internal energies.
2. There are various opportunities for distributions with various energies, i.e. various thermodynamic probabilities.” What this means is the more the thermodynamic probability, the more are various states with internal energies.

In other words, as the result of mixing, additional energy levels appear – splitting (expansion) of electron levels - (their creation wastes energy), which are then filled (energy emission). These processes are connected with the heat oscillations of atoms. As he writes further: “Every disorder is connected to the absorption of heat energy, defining in that way the heat capacity (heat disorder)”

Thus, Cottrell attempted to show the way to answer the connection between mixing entropy and the energy and with vibrational entropy.

If we expand the Cottrell’s version, we find out that in mixing there are two processes occurring simultaneously in opposite directions: heat energy absorption through the internal work that increases heat capacity and energy emission through the electrons transfer to the lower energy levels.

Let’s try and review these interconnections to find out their physical meaning.

7. Connection between entropy and average heat capacity

After all, how does the effect defined by a number of distributions, connect to the energy? How is mixing entropy connected to the energy of interatomic oscillations?

Every disorder is connected to the heat energy absorption, defining the heat capacity (heat disorder) [19]. In thermodynamics, entropy, first of all, expresses *the energy of thermal atomic oscillations* and, therefore, depends on temperature. The higher the temperature, the higher is amplitude and the energy of atomic oscillations and, therefore, entropy. Thus, *entropy can be expressed through the specific heat capacity* **Cp** *or, as it is also called, vibrational heat capacity:*

$$\mathbf{S= Q/T={}_0\!\int^T dQ/T = {}_0\!\int^T CpdT/T=\hat{C}} \quad (11)$$

But the average (not specific) heat capacity **($\hat{C}$),** is determined by the same formula.. Therefore, we see that entropy is equal to the average heat capacity. But the average heat capacity, in contrast to the abstract concept of entropy has a real meaning and can be calculated. Because the mixing entropy is included in the united definition of entropy and, as we showed earlier, can do work, i.e. it is connected to the increase of atomic vibrational energy, it is also equal to the change of average heat capacity.

$$\Delta \mathbf{S_{mix}= \Delta\hat{C},} \quad (12)$$

The average heat capacity and entropy being expressed by the same formula is noted in many works. This coincidence was just ignored by the traditional thermodynamics. But this particular context defines the physical meaning of any entropy as an energy capacity. Energy, first of all, is thermal oscillations of atoms. Returning to the classical definition of entropy by Cottrell - *«the system with absolute temperature T absorbing an infinitely small heat value and not changing in any other way»* **$dS=dQ/T$**, it is clear, that in order to absorb heat and not increase its temperature, the system just needs to increase its capacity. In our case, the average heat capacity.

It should be noted, *that when we talk about mixing, we don’t just mean only the liquid and solid solutions, forming at mixing, but also multiphase structures, including eutectic ones, forming at* *crystallization - since vibrational energy and entropy, as would be shown in the third part of the book (look table of contents), remain in the system, despite the separation of homogeneous mixture.*

On fig.8 there is a graph of specific heat capacity in relation to the reduced temperature, particularly – the relation of Debye temperature to the common one. The space under heat capacity curve defines enthalpy or heat inserted to the system. By dividing it by the temperature range from zero degrees Kelvin we get the value of vibrational entropy S_{vib} , equal to average heat capacity.

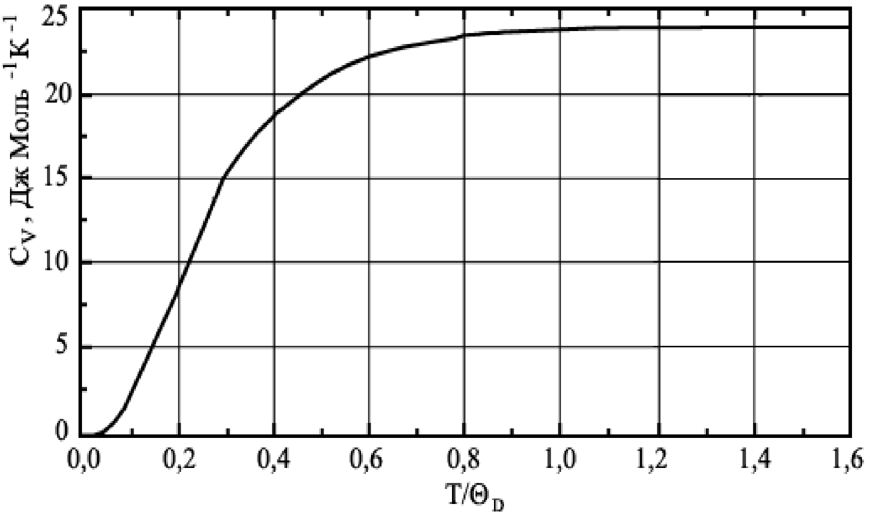


Fig. 8. Heat capacity $C_V(T)$ *dependence, calculated in the Debye model. X-axis is reduced temperature* T/Θ

8. Hidden (latent) processes in mixing

But where is this vibrational energy hidden and by what does the average heat capacity increase?

We don't observe the heat effects at ideal mixing, but in reality they exist, yet occurring in the opposite directions inside the system. The system releases energy and, by simultaneously shifting (rearrange itself) and increasing its capacity, absorbs heat. These processes occur even during the formation of the ideal mixture, *where the **A–B, B–B** and **A–A** bonds are identical and thus, we can't see any heat effects during mixing. But in reality, 2 hidden (latent) processes occur at the same time and compensate each other:*

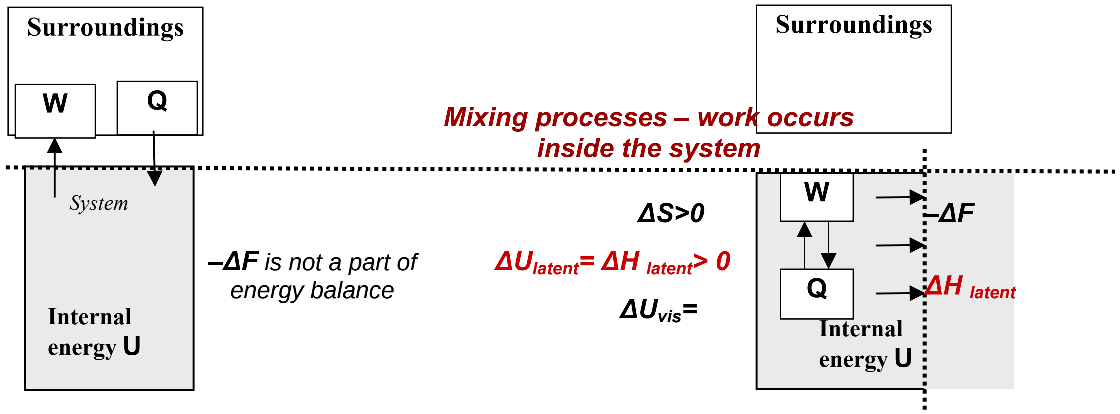
1. The increase of average heat capacity, requiring heat absorption to support the constant temperature.

2. At the same time, hidden heat emission, $\mathbf{Q = \Delta\hat{C}T}$, *through the strengthening of interatomic bonds.*

The second process is required to comply with the first law of thermodynamics or the energy conservation law. There is a work being done to increase average heat capacity, i.e. the energy of atomic oscillations, but the internal energy under ideal mixing, does not show any heat effects. But in reality, the energy processes occur, as presented in fig. 9.

Figure 9 is explained by the first law of thermodynamics $\mathbf{\Delta U=\Delta Q-\Delta W}$. Under ideal mixing $\mathbf{\Delta Q=0}$ and $\mathbf{\Delta F= -\Delta W}$ like in Cahn's interpretation (see ch. 3). As a result, we get $\mathbf{\Delta U= -\Delta W= \Delta F}$, described on fig. 9b as the increase in internal energy $\mathbf{\Delta U}$ or enthalpy $\mathbf{\Delta H}$ (under constant pressure) during mixing. Because the work was not done on the environment (no observable heat effects), but left inside the system, it causes the internal energy increase.

This new graphic presentation the second law of thermodynamics for irreversible processes provides a physical and energy representation to such abstract terms like mixing entropy and free energy. With that, our approach is based only on the classic interpretation of the second law of thermodynamics, which was simplified by the traditional thermodynamics. As a result, many hidden processes occurring in opposite directions have been left ignored.



a

b

Fig. 9.Graphic presentation of the second law of thermodynamics in the ideal mixing: a – traditional view (free energy is not a part of energy balance – no internal energy change and heat effects, therefore not corresponding to the first law of thermodynamics [4]; b – according to classic thermodynamics (Cahn), where statistical entropy is identical to formal entropy. Internal energy increase through the increase of heat capacity (mixing of the components) – the system did work to increase heat capacity - average heat capacity and simultaneously filled it with thermal energy. With that the internal energy value has increased [6, 7]

Let's look at these two processes in detail.

8.1. Average heat capacity increase through the decrease of Debye temperature and heat absorption during mixing

Usually, it is considered that during the transition from atoms to a homogeneous mixture the specific heat capacity, and, therefore, vibrational entropy, according to the additive rule of Neyman-Kopp, does not change. But it is not completely true. The Neyman-Kopp rule is applicable mostly to some types of alloys with intermetallic compounds, under the temperatures not higher than Debye temperature. By using the Neyman-Kopp rule, the deviation from actual value can reach 8%, which would cause the change in enthalpy for 2 kilojoules/mole at average specific heat capacity 25 joules/mole under 1000 degrees Kelvin. It is a significant value, comprising almost 25% from the average alloy melting temperature. But even higher change in enthalpy occurs under the shift of the heat capacity curve to the left (fig. 10) [6, 7].

Shift of Debye temperature to the left causes a significant increase of average heat capacity of the the system, and, therefore, energy and amplitude of the atomic oscillations, correlating with Cottrell's approach. On figure 10 this area, characterizing energy, is crosshatched. This is the area between the curves of heat capacity before mixing – where the heat capacities of original components add to each other, – and after mixing. It should not be ignored, because the decrease of Debye temperature leads to the decrease of melting temperature, and the decrease of melting temperature is observed in all mixing processes: formation of solid solutions or eutectics, because the processes are accompanied by the increase of free energy through the increase of mixing entropy according to the second law.

Neyman-Kopp himself noted, that his method cannot be used at temperatures lower than Debye temperature as well as for the average heat capacity calculations – because the formation of alloys, especially eutectic ones, is accompanied by the decrease of *melting temperature and, therefore, Debye temperature [31].*

Dehlinger noted, that, if according to the Neyman-Kopp rule, the heat capacity of lattice oscillations in observable compositions is additive (is a linear function independent from the current component), the vibrational entropy becomes equal to zero, which is allowed as approximate value [30]. But the physical properties of such mixture – for example, melting temperature, - should not change, which does not occur in reality.

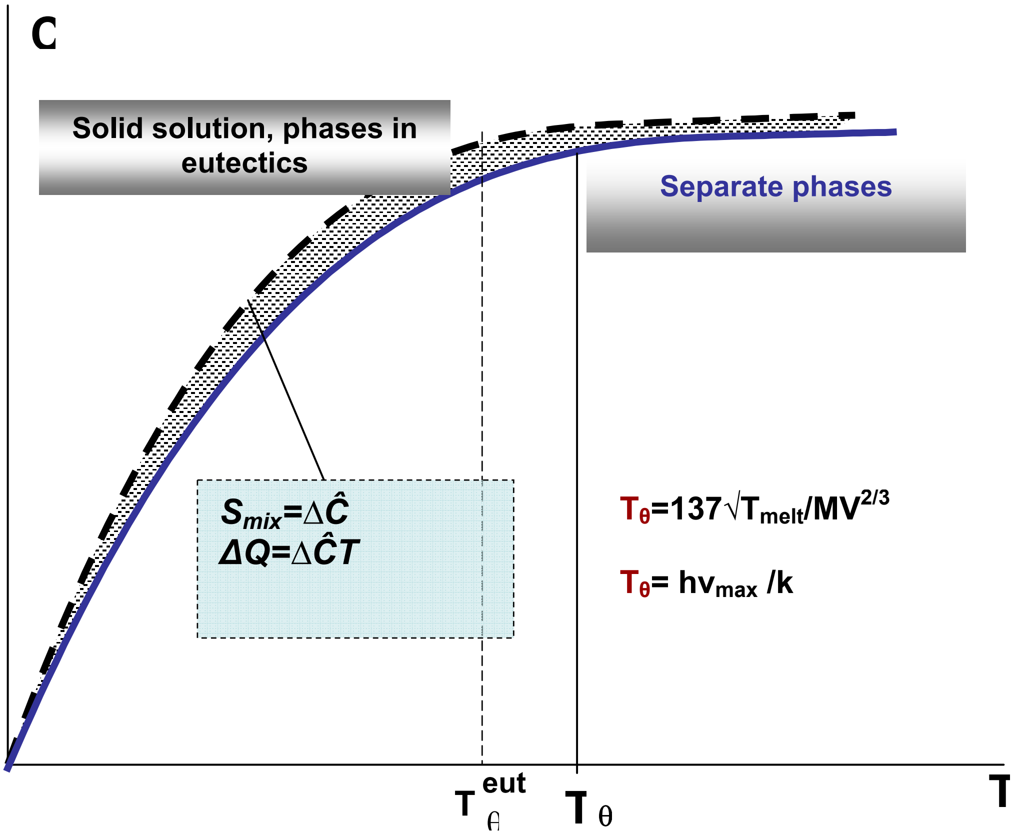


Fig. 10. Change of specific heat capacity in ideal mixing, solid curve – original isolated phases (average reduced value), dotted curve – solid solution [6, 7]

But aside from Neyman-Kopp method to calculate heat capacity, there is also the Debye method based on the oscillation energy. It is described in many thermodynamics and alloy physics textbooks, particularly, in the book by Swalin - «Thermodynamics of Solids» [4]. Original data for calculations is provided by reduced forming alloy elements temperatures and by the melting temperature of the elements and alloy itself. Based on the melting temperature for alloy, its Debye characteristic temperature is calculated by the Debye formula:

$$\theta_D = \theta'_D\sqrt{T'_{melt}}/\sqrt{T_{melt}} \qquad (13)$$

where θ_D and θ'_D - Debye characteristic temperature of the alloy and original components, T'_{melt} и T_{melt} - melting temperature of alloy and original components.

Then, in the Debye functions table the heat capacity of elements forming alloy is found, then summed them up to determine the united heat capacity for alloys. It is clear that the heat capacity of elements in the alloy turns out to be lower than additive, according to Neyman-Kopp method. Therefore, the entropy is higher and free energy of alloys is always lower.

So, under ideal mixing, alloy has a lower Debye temperature, but higher specific and average heat capacity, i.e. the entropy and the energy of atomic oscillations are higher, proving the Cottrell's point regarding the atomic heat oscillation energy increase at components mixing and the match between mixing entropy and vibration entropy.

From this, we can come to another important conclusion. Because the Debye temperature applies to the solid state, where alloy can be not only in a homogeneous state, but also in separate phases under crystallization, the change in alloy's heat capacity (in contrast to the additive heat capacity of components or phases) can be applied to heterogeneous systems (not only solutions). Even while formally, mixing entropy disappears in crystallization, its vibrational energy remains. Therefore, mixing entropy transforms into oscillation (vibrational) entropy. This conclusion is important for studying the phase equilibrium, where the change of vibrational entropy during the transfer from mechanical phase mixture to an alloy is considered to be zero.

Therefore, in mixing processes the average heat capacity of alloys increases due to the shift of heat capacity curves to the left – decrease in Debye temperature.

The heat capacity theory from the point of molecular kinetic theory of atomic oscillations in a crystal lattice was developed by Debye and Einstein. According to their approach, heat capacity increases to the Debye temperature due to the increase in the frequency of atomic oscillations up to a maximum frequency ($\mathbf{v_{max}}$), specific to this metal crystal lattice. Heat capacity over the Debye temperature increases due to the increase in amplitude of atomic oscillations, becoming approximately 3R value. When oscillation amplitude reaches around 8-10%, according to the Lindemann's rule, the crystal lattice can't hold the thermal oscillations and destroys – the metal or alloy melts down.

Therefore, the maximum allowed oscillation frequency of harmonic oscillators is proportional to the Debye temperature ($\mathbf{T_\theta}$) under the following formula:

$$\mathbf{T_\theta = hv_{max} /k} \qquad (14)$$

where **k** – Boltzmann constant

Debye temperature, along with maximum oscillation frequency, is proportional to the square root of melting temperature:

$$\mathbf{T_\theta =137\sqrt{}T_{melt}/MV^{2/3}}, \qquad (15)$$

which also includes atomic weight **(M)** and atomic volume **(V)**, that remain unchanged in the alloy formation.

Therefore, the lower is maximum oscillation frequency and Debye temperature, the lower is melting temperature. It is a known statement, but here it is viewed in detail, due to its importance in understanding the physical meaning of entropy.

Another proof of the increase in average heat capacity during mixing due to the reduction in Debye temperature and maximum atomic oscillation frequency can be found in the book by Swalin - «Thermodynamics of Solids», where he tries to describe the effects that cause the decrease in maximum oscillation frequency of the crystal lattice [4].

Swalin studies the ideal crystal lattice with implemented foreign atoms (fig. 11). He writes: *«Every atom oscillates near its place. If a foreign atom is introduced into crystalline lattice, the disorder arises and, therefore, the entropy proportional to the atom oscillations amplitude. Thus the oscillation amplitude would be bigger than in the ideal lattice of the crystal. The defect would affect the oscillation frequency of nearby atoms. As the result there would be a decrease of maximum allowed frequency of harmonic oscillators, allowing the positive vibrational entropy, connected to this defect».*

Further he writes: *"The introduction of dissolved atom into crystal lattice decreases the oscillations frequency of nearby atoms in dissolved solution and makes a positive contribution to the vibrational entropy.* ($\mathbf{\Delta S_{vibrational}}$)*."*

As known, Debye temperature is proportional to maximum oscillation frequency, and also depends on melting temperature, i.e. the less is maximum oscillation frequency in a crystal, the less is melting temperature (formulas 14 and 15).

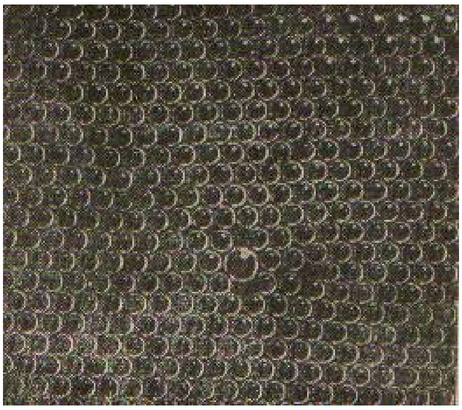


Fig. 11. Bubble model of impurity atom in a crystal [4]

Therefore, it is made clear, that during the formation of solutions as well as the alloy crystallization (when phases are formed), vibrational entropy or average heat capacity increase in comparison to the original components due to the melting and characteristical temperature change and the change in the energy of atomic oscillations. In other words, each phase in alloy structure, depending on its composition and melting temperature, has its own oscillation mode type, entropy and free energy in distinction from taken separately. This leads to the fact, that in viewing the phase equilibrium by geometric thermodynamics (Gibbs equilibriums), free energy values would depend from the composition i.e. from the ratio of phases in alloy. Therefore, we can't treat phase equilibrium as mechanical phase mixture, as it is accepted now, i.e. ignore the change of vibrational entropy in relation to the melting temperature.

8-2. Hidden heat emission during mixing due to strengthening of interatomic bonds

Let's take a look at the second process, the one that occurs with interatomic bonds during mixing and the creation of solid and liquid solutions. Because during the ideal mixing the average heat capacity increase, the system must absorb heat and cool down, but we don't observe the heat absorption during ideal mixing, i.e. when atoms A and B are equal in their properties.

The fact is that at the same time with heat absorption, the heat emission occurs due to strengthening of interatomic bonds. These processes oppose and compensate each other, thus we can't observe them. Strengthening of interatomic bonds at mixing is similar to the mechanism of formation metallic bond in metals and alloys.

The mechanism of metal bond formation due to splitting of valent electrons levels is known (fig. 12). Cottrell [19] writes: *«When two or more atoms come near each other, energy levels split at levels covering each other. The number of splitting levels (or quantum states) is equal to the number of atoms».*

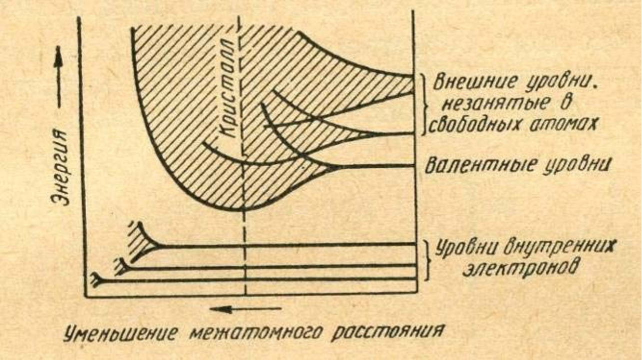


Fig. 12. Atomic energy levels expansion when atoms come near to the crystal border [19]

When foreign atoms are inserted into metal, an additional split of energy levels for valent occurs, as shown on fig 12, and the width of the energy strip increases. It does not mean the common chemical bond between nearby atoms, for example, **A** and **B**, which is already accounted for and, regarding of the connection nature, causes its strengthening or weakening, which does not change its bond energy during ideal mixing. It means the additional collective interatomic bond, analogous to the metal bond in a crystal lattice. With that the valent electrons go to the lower levels, the atomic bond strengthens and the energy is released, ***compensating*** the increase of average heat capacity.

Cottrell creates a physical view of this collective bond: *«in a crystal, all atoms «feel» each other and every single atomic and energy level creates a quasi-continuous shelf of levels» [19].*

Therefore, Cottrell shows that this bond is applied to the whole crystal. This is our case of solid and liquid solutions. But it may be presumed that even in the heterogeneous structure the metal bond can transfer to the nearby phase, if the phases **are mutually oriented** to make a bond through the valent electrons level expansion, as will be shown in the third part of the book (fig. 13).

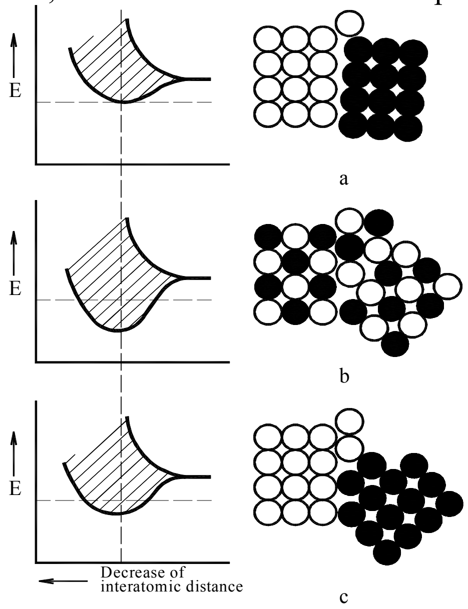


Fig. 13. Atomic energy level expansion (A atoms) of valent electron area during the formation of: a) original isolated phases; b) melting; c) eutectic phases [7, 8, 32-34].

This additional bond type, previously unaccounted in alloys, can be nominally called **Interphase Metallic Bond** - IMB, one of parts in a common interatomic bonds.

Of course, there is not a lot of ideal mixtures in nature. Generally, during mixing we see either positive mixing enthalpy (through heat absorption, when the bonds **A–A** and **B–B** are stronger than **A–B** bonds), natural for many solid solutions, or negative (heat emission, when **A–A** and **B–B** bond**s** are weaker than **A–B** bonds), natural to the eutectic alloys with intermetallids. But the noted regularities of strengthening interatomic bonds and the increase of average heat capacity remain. They just get additional parameters, strengthening or weakening these effects.

Therefore, *in case of real mixtures, the resulting action will be naturally defined not only by a mixing entropy value, but the value of free energy change itself.*

The scheme for real mixtures is presented on the fig. 14. *Internal energy value after mixing is shaded blue and limited by a vertical dotted line. Free energy value change is crosshatched.*

In negative energy mixing, with more strengthened bonds of unlike atoms (**A-B**) than the similar ones (**A–A and B–B**), the atomic bonds additionally strengthened and energy was released into the environment. One would think It should be less of it in the alloy – but the internal energy of an alloy may still increase if the entropy part contribution $\mathbf{T\Delta S_{mix}}$ prevails (fig. 13a). The decrease of free energy in this case is more significant than during the ideal mixing, because $\mathbf{\Delta H}$ ***and*** $\mathbf{T\Delta S_{mix}}$ work in one direction. Therefore, in such mixing there is a sum of interatomic bond strengths due to two processes in the same direction moving.

If the mixing process occurs with heat absorption, when the energy of **A–B** bonds is less than **A–A and B–B** (fig. 13 b), internal energy additionally increases more than during ideal mixing (to the entropy part contribution **$T\Delta S_{mix}$** another one is added - **ΔH**). But in that, the free energy decrease occurs less than during the ideal mixing and the strengthening of interatomic bonds is lower too.

In other words, internal energy and free energy stay in the counterphase. The more heat the system can absorb under the current temperature - to increase the energy of atomic oscillations - the less is strengthening of interatomic bonds.

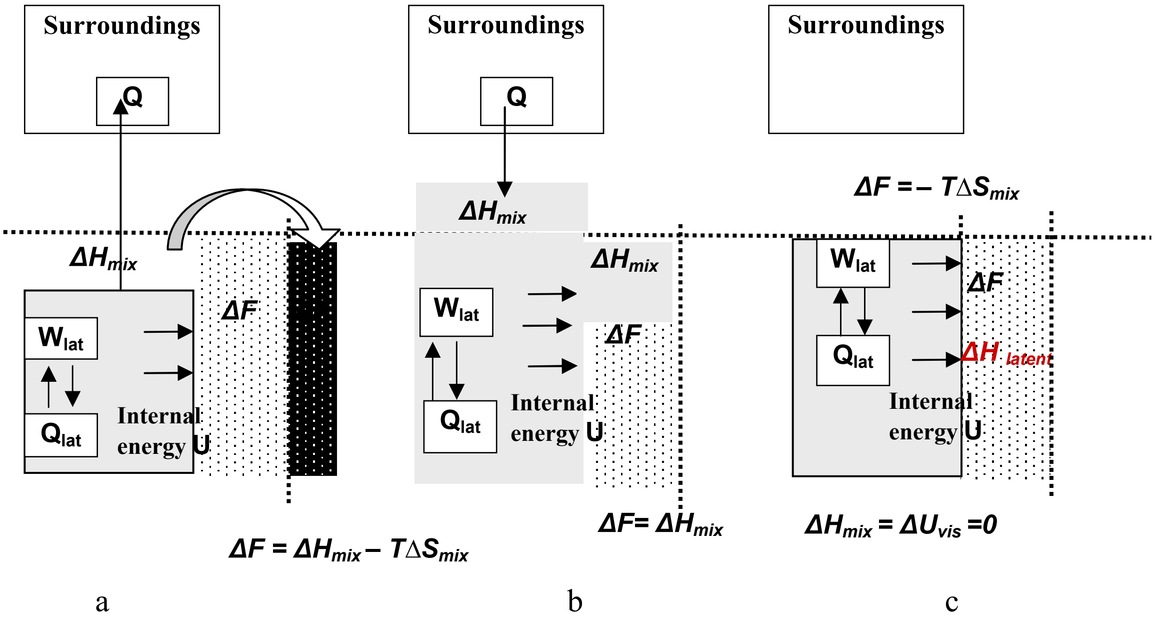


Fig. 14. Graphic presentation of the second law of thermodynamics in case of real mixing, a) – negative energy (enthalpy) mixing (heat emission during mixing ΔH<0), b) – positive energy (enthalpy) mixing (heat absorption during mixing ΔH>0), c) – ideal mixing (ΔH=0) - resulting increase of internal energy corresponds to the value change of free energy *<u>ΔF. Internal energy value after mixing is shaded blue and limited by a vertical dotted line. Free energy value change is crosshatched.</u>*

8-3. Enthalpy change during mixing

Therefore, two energy processes, occurring during mixing, go simultaneously and compensate each other: energy emission u increase average heat capacity. Because of that, they are hard to observe under temperature measuring, i.e. in a short temperature range (as heat capacity is usually measured).

Main change goes under Debye temperature (T_Θ). But if we measure and then compare the alloy and its components enthalpies from zero degrees Kelvin, we can detect this difference.

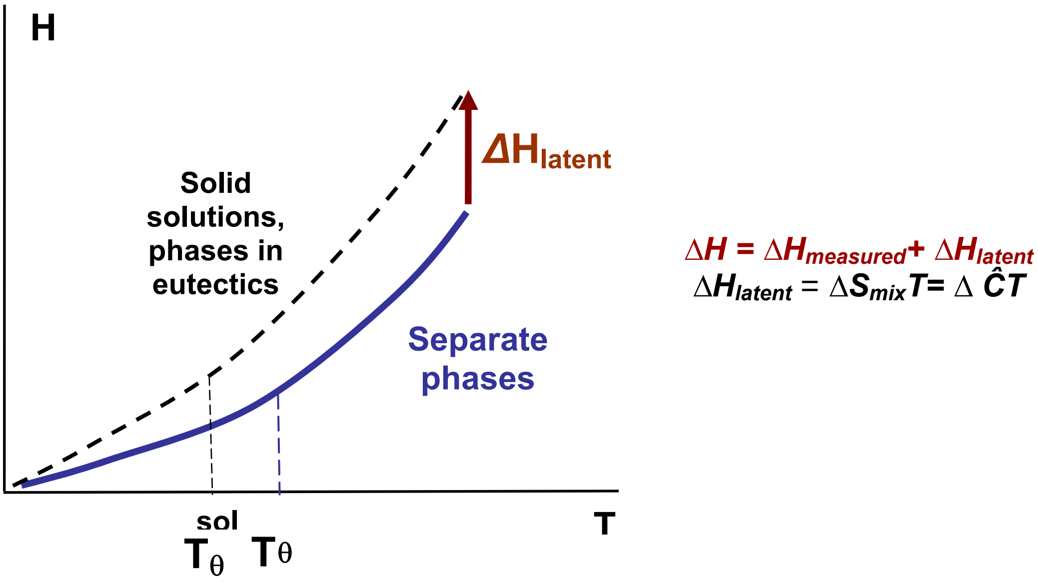


Fig. 15. The change in enthalpy in versus temperature during the formation of ideal mixture (black dotted line) from the mechanical mixture of original components-phases (solid blue line – reduced average values)

Fig. 15 schematically illustrates the dependence of enthalpy H under constant pressure for alloy and its original components (mechanical mixture). In accordance with to the change of heat capacity (fig. 8, 10), the enthalpy during heating increases slowly until reaching Debye temperature, then faster and, starting from some point, almost linearly.

Enthalpy increase in solid solutions and alloys compared to the original components correlates to the corresponding heat capacity graphs in fig. 10. Thus enthalpy value in alloys will be higher by ΔH_{latent} , depending on the mixing entropy change $\Delta S_{mix}T$ or average heat capacity change $\Delta\hat{C}T$. Therefore the united enthalpy value for alloy $\Delta H_{\sum}$ in fig. 14 would consist of visible, i.e. measured value $\Delta H_{measured}$ (zero for ideal mixture), and latent (hidden) enthalpy ΔH_{latent}, spent to increase the average heat capacity of alloy. Generally, it can be explained in simple formulas:

$$\Delta H_{\sum} = \Delta H_{measured} + \Delta H_{latent} \qquad (16)$$

$$\Delta H_{latent} = -\Delta S_{mix}T = \Delta\,\hat{C}T \qquad (17)$$

Negative sign (minus) underlines the energy emission, absorbed then by the increase of average heat capacity $\Delta\,\hat{C}$.

Now the traditional free energy equation for *reversible and irreversible* processes looks like this:

$$\Delta F = \Delta H_{measured} - T\Delta S \qquad (18)$$

For *reversible* processes:

$$\Delta F = \Delta H_{measured} \qquad (19)$$

To our opinion for *irreversible* processes the second law of thermodynamics can be simplified, because $T\Delta S = -\Delta H_{latent}$ and, using the formula (19), we get as a result:

$$\Delta F = \Delta H_{measured} + \Delta H_{latent} = \Delta H_{\sum} \qquad (20)$$

In such way the physical meaning of the second law of thermodynamics expresses itself for irreversible processes – *mixing or diffusion*. *All hidden work of the* process is spent to the increase of average *heat capacity* (internal energy) of the system by increasing the vibrational energy, as proven by Kozyrev experiments and our weight measuring experiments [21, 22, 26].

Therefore, the second law of thermodynamics can be considered as a law of energy conservation, because it reveals the hidden energy processes, occurring inside the system.

9. Conclusion

1. Statistical (mixing) entropy is identical to the vibration entropy, has an energy context, expressed through the change in the nature of atomic oscillations, can be expressed also as dQ/dT, which is proven, in particular, by osmotic processes.

2. In Cahn's interpretation of the second law of thermodynamics Helmholtz free energy is defined as a work, or amount of energy taken with opposite sign, that could be potentially performed or dissipated by the system. The main contribution to the free energy value change is made by the entropy part of equation TS, hence, entropy of mixing that has an energy meaning.

3. Mixing entropy can do work. Mixing process are hard to observe because they occur inside the system and are accompanied by the increase of average heat capacity due to the decrease of Debye temperature, which, according to Lindemann's rule, lowers down the melting temperature; For heterogeneous systems, especially esthetics ones, this leads to the lowering of a melting temperature and change in average heat capacities for esthetic phases in comparison to the original state (mechanical phase mixture).

4. Even in an ideal mixing, two hidden (latent) processes go on at the same time and compensate each other. First - the increase of average heat capacity, requiring heat absorption to support the constant temperature. Second - at the same time, latent (hidden) heat emission (release), $Q = \Delta\hat{C}T$, or hidden enthalpy increase, through the strengthening of interatomic bonds, particularly in high-entropy alloys (HEA).

5. The second law of thermodynamics can be considered as a law of energy conservation, because it reveals the hidden energy processes, occurring inside the system.

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Part 2. Entropy effects in real systems

It is the **second part** *of a united article: "Hidden» thermodynamics – rational approach to known facts" published in J. Atomic Strategy, S-Petersburg, in three articles (3 Parts - Russian version):*

1. The discrepancy between the approaches to the second law of thermodynamics and phase equilibrium. Solid and liquid solutions, Issue 109, December 2015, 17-23, *available online* http://chronos.msu.ru/images/rreports/Savchenko/Savchenko_Skrytaya_termodinamika_trezvyy_vzglyad_na_izvestnye_veshchi.pdf

2. Entropy effects in real systems,. Issue 110, January 2016, 14-19, *available online* http://chronos.msu.ru/images/rreports/Savchenko/Savchenko_Entropiynye_effekty_v_realnykh_sistemakh.pdf

3. Entropy effects in multiphase systems. Phase diagrams and eutectics melting mechanism, Issue 111, February 2016, 28-33, *available online* http://proatom.ru/modules.php?name=News&file=article&sid=6484

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10. Introduction

This is a continuation of a previous article on the subject of thermodynamics [1] (the second part of of three).

The second part deals with the practical usage of described approaches to the real systems – high-entropy alloys, corrosion-resistant iron (non-rusting iron), transformations in actinide systems, the possibility of the second type "perpetual mobile" creation, etc.

Our approaches develop the forgotten and incorrectly interpreted postulates of classical thermodynamics, summarized in the first part and in [2-4]. Briefly:

- Statistical (mixing) entropy *is identical to the vibration entropy, has an energy context, expressed through the change in the nature of atomic oscillations, can be expressed also as* ***dQ/dT****, which is proven, in particular, by osmotic processes;*
- *In Cahn's interpretation of the second law of thermodynamics Helmholtz free energy is defined as a work, or amount of energy taken with opposite sign, that could be potentially performed or dissipated by the system. The main contribution to the free energy value change is made by the entropy part of equation TS, hence, entropy of mixing that has an energy meaning;*
- *Mixing entropy can do work. Mixing process are hard to observe because they occur inside the system and are accompanied by the increase of average heat capacity due to the decrease of Debye temperature, which, according to Lindemann's rule, lowers down the melting temperature;*
- *Even in an ideal mixing, two hidden (latent) processes go on at the same time and compensate each other. First - the increase of average heat capacity, requiring heat absorption to support the constant temperature. Second - at the same time, latent (hidden) heat emission (release),* $Q = \Delta \hat{C}T$*, or hidden enthalpy increase, through the strengthening of interatomic bonds;*
- *The second law of thermodynamics can be considered as a law of energy conservation, because it reveals the hidden energy processes, occurring inside the system.*

11. Strengthening effects of interatomic bonds during the formations of solid solutions (High-Entropy Alloys - HEA)

There could be found many experimental proofs of the developing model for the energy nature of mixing entropy and strengthening interatomic bonds under the formation of solid solutions. For example, recently a new class of alloys was discovered, called high-entropy alloys, or superalloys for their properties. They form on the base on the maximum entropy rule with the usage of "entropy force" concept, the physical meaning of which is still not fully understood, because the mixing (statistical) entropy has never been associated with energy, only as a range of disorder [5-8].

Unlike classical alloys, that have basis-element and alloying elements, high-entropy alloys consist of a significant number of elements (from 5 to 12-15) mostly in equal parts. Small amounts of metalloids can be added too [6, 7].

Main role in determining the structure and properties of such alloys is played by configurational (mixing) entropy.

It is known, that Gibbs energy, determining the system stabity, is defined by an equation:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (21)$$

These alloys have mostly small positive mixing energy, which should decrease the stability of a solid solution. But due to the high disorder and high configurational entropy, a solid solution is formed based on the crystal lattice (fcc or bcc). Under high temperatures this energy **($T\Delta S_{mix}$)** is closer to the enthalpy of intermetallic bonds formation and, therefore, supresses the possibility of their formation. Naturally, just the entropy contribution defines the alloy properties.

Mixing entropy in multicomponent systems is determined by the following formula:

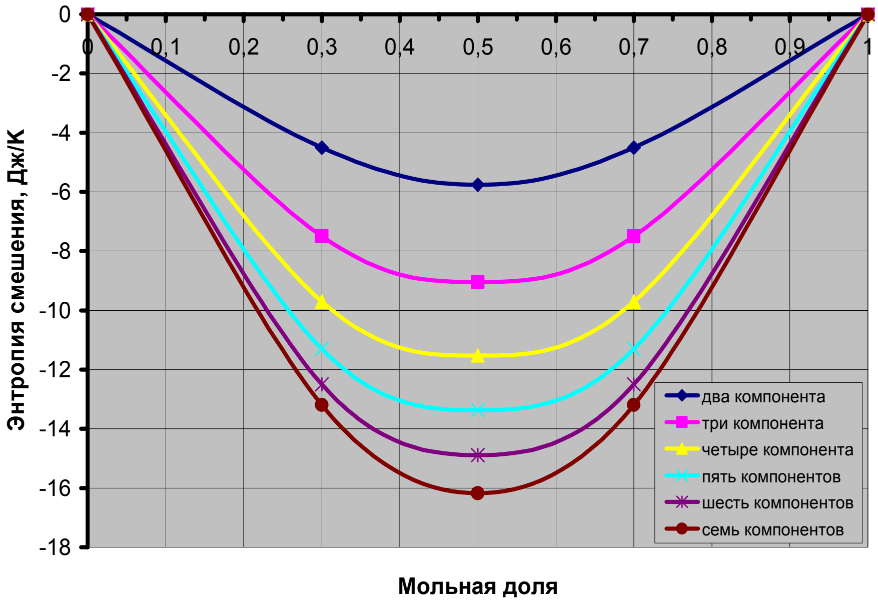
$$\Delta S_{mix} = - R\sum X_i \ln X_i , \qquad (22)$$

where X_i – molar part of the component in an alloy

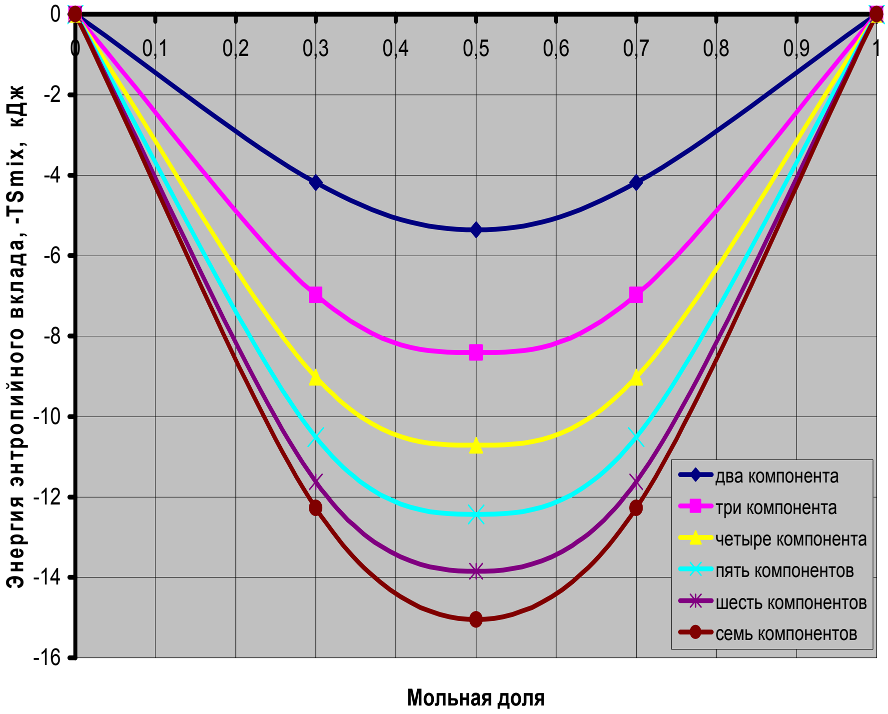
Fig. 16a illustrates the mixing entropy change versus the number of components in accordance with the formula (22). For simplicity, the molar parts of the components are taken in equal measures. It is seen, that in the transfer from a two-component to seven-component system, the mixing entropy increases almost by 3 times, same goes for its energy contribution - **$T\Delta S_{mix}$.** This contribution is enormous. For example, at temperature 930^0K (average operating temperature for steel claddings in fast reactors and melting temperature of aluminum) it reaches 5,35 kilojoules/mole for a double component system, which is half from the melting enthalpy of aluminum (fig. 15 b). For the system of seven equal components, the energy of interatomic bonds through the entropy contribution is 15 kilojoules/mole, which is comparable to the enthalpies of formation and melting of intermetallic phases and chemical compounds. Thus, it is clear, why high-entropy alloys have:

1. Such high thermodynamic stability of solid solution.
2. High strength, high-temperature strength, heat and corrosion resistance.

Naturally, these properties would be defined by the free energy change value, which is also influenced by mixing energy (enthalpy). Slightly positive enthalpy value, natural for many solutions, somewhat lessening this effect. But entropy contribution is the most defining one here.



a



b

Fig. 16. Entropy change curve at mixing of two to seven components in equal parts (a) and energy contribution of mixing entropy (-$T\Delta S_{mix}$) at temperature 930^0K (b)

Currently, the existing high-entropy alloys could be nominally classified in 3 groups:

1. Alloys based on Fe, Ni, Co, Mn, Cr, V, Mo, Al, Ti, Cu and others.
2. Alloys based on refractory metals Nb, V, Mo, Ta, W, Re, Ru and others.
3. «Light» alloys based on Al, Mg, Be, Ti, Si and others.

Based on the formation principles for high-entropy alloys, an actinide group could also be added to these. Those are alloys based on uranium, plutonium and torium with neptunium, americium, actinium, curium etc., which can form continuous solid solutions, and also alloys alloyed additionally by molybdenum, zirconium, niobium, titanium etc., stabilizing the bcc crystal lattice. Alloys of that type, particularly based on U-Pu-Zr, are very promising as metal fuel for fast reactors. Their properties can be significantly improved by using this approach.

The unique nature of high-entropy alloys is that they have high tensile strength, heat and corrosion resistance in different environments. With that, their properties improve, compared to the analogues – simple solid solutions with strengthening intermetallic phases.

From the classical theory point of view, the strength of interatomic bonds, defined by mixing enthalpy (not entropy), should decrease (energy absorption occurs due to the weakening of interatomic bonds) and alloys should not have such high properties. Thus, their properties are being explained by the formation of hypothetical nanostructures or amorphous phases.

In actuality, this effect is explained by the strengthening of interatomic bonds at the increase of configurational entropy, overlapping the bond weakening effect due to the positive mixing enthalpy value.

Resulting bond strength value would be determined by the free energy change value, in this case equal to the to the energy increase of interatomic bonds. By following this rule, it is easy to calculate the optimal composition for high-entropy alloys in different systems.

Therefore, in alloying one should not only consider the maximum number of alloying components, which energy contribution to the strengthening of interatomic connection could be calculated by Gibbs-Helmholtz potential change, but also the addition of elements with a higher negative mixing energy. First of all, it is Al, Si, C, B, Ti, P etc. in various combinations. Their dissolution would be higher due to the solution stabilization by configurational entropy.

12. Thermodynamic database and phase equilibrium calculations (Thermocalc, CALHAD)

Separately, we can note the use of new approaches to modify the thermodynamic databases and programs, like CALPHAD (CALculation of PHAse Diagrams) and Thermo-Calc, used to describe phase equilibriums and to build state (phase) diagrams [10, 11].

Phase diagrams are a strong instrument used to predict the system state under different conditions. Phase diagram (diagram for chemical system composition dependence on temperature) indicates the existence areas of compounds (phases) and solutions. The CALPHAD approach is based on the fact that phase diagram is an expression of equilibrium balance of important thermodynamic properties of the system, compiled from phase properties. Therefore, phase diagram can be calculated by a preliminary evaluation of thermodynamic properties of all phases, composing the system [12, 13].

The main approach – finding out a realistic and reliable math model for Gibbs energy in each phase, which depends on the other system properties: heat capacity, entropy, interatomic bond energy, enthalpy etc. Because these values require correction based on the energy interpretation of configurational entropy, such corrections should be applied to the calculation programs, which should be modified with additional properties, such as, for example, the interatomic bonds energy change. These additional parameters can improve the prediction of alloy composition and properties.

Should be noted, that despite the widespread advertisement of these thermodynamic system calculations, popular articles and talks regarding them, their accuracy is fairly low. If the calculations are not preceded by experiments, their results turn out to be inaccurate, at best. Example from my own experience. When I needed to correct the composition of zirconium matrix alloys during the development of dispersion-type fuel compositions in order to determine an eutectic point, I referred to the very high-level specialists who used verified CALPHAD and Thermo-Calc programs. Because there had not been a lot of data for triple and quadruple phase diagrams in this field, the calculations were mostly made based on the double state diagram with the usage of thermodynamic math models. As a result, neither formed phases, nor eutectic melting temperature, nor eutectic point reflected reality. Worst of all, the result turned out to be less accurate than my own scientific intuition (I have predicted eutectic point and melting temperature right, made a small mistake in phases). What math apparatus can even predict, based on just the traditional thermodynamics, the eutectic point of 790 degrees for a zirconium based alloy with melting temperature 1860 degrees Celsius. After that, additional alloying with titan, that eutectic point was decreased to 690 degrees, close to aluminum melting temperature [14-16].

It is not that the CALPHAD and Thermo-Calc methods are bad, they are just usually based on the incorrect thermodynamic principles, the math replaces the real physical meaning of processes and phenomena. Therefore, additional thermodynamic data and formulas should be added to the program. For example, the database of components and phases should consider the Debye temperature. Phase heat capacity calculation should be calculated by Debye method, not by the Neyman-Kopp rule. Include the average heat capacity values into database, its change at mixing, as well as its difference between original components and an alloy, determining the interatomic bond strength, etc. Corresponding changes should be made to calculation formulas.

As noted in advertisement: «The power of CALPHAD method is in the united description of subsystems comprising a multicomponent system». But such unification should not be done without considering internal thermodynamic connection between phases – this will be shown in the third part of this book. We have described single-phase systems formed by solid and liquid solutions. Further we will show that at crystallization, where the homogenous mixture divides into heterogeneous solid phases, the average heat capacity and mixing entropy don't disappear but transform into vibrational entropy. Therefore, our approach is applicable to describe the multi-phase systems and phase equilibriums, where currently the vibrational entropy change is considered to be zero.

13. Explanation of anomalous in actinide systems behavior as configurational entropy changes during heating and microalloying

Actinides (Th, U, Pu, Np, Am and others) are among the most difficult metals to study because of their complicated electron structure. At the same time, their usage as nuclear fuel as well as in closed nuclear fuel cycle is required for successful development of nuclear energy. [17].

Here are some unusual properties of plutonium, one of actinides:

1. Very low melting temperature.
2. Volume decrease during melting.
3. High anisotropic thermal expansion ratio.
4. Six phase changes in a solid state.
5. Lowest density in the highest-density phase.
6. Anomaly high heat capacity at temperatures close to the absolute zero etc. [17-20]

These and other unusual properties are partially illustrated on figure 16, taken from the S. Hecker review [17].

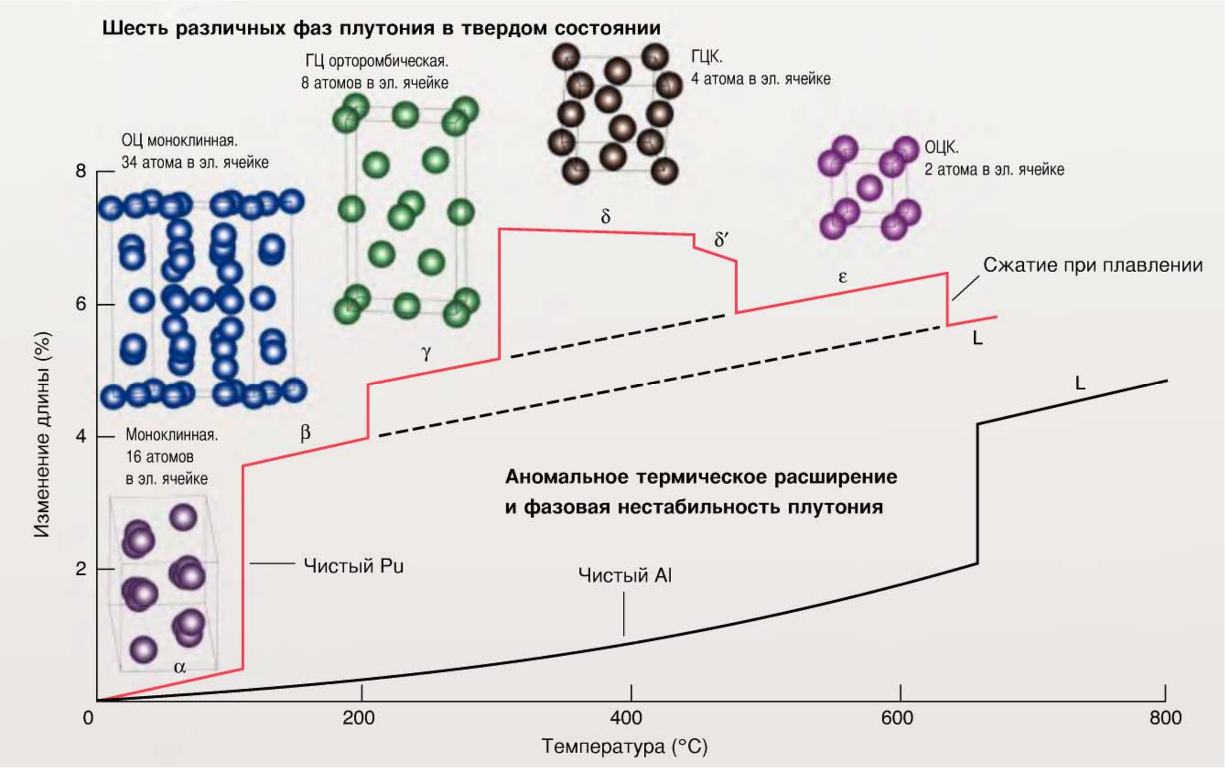


Fig. 17. Physical properties of plutonium [17]

Most interesting from the practical point of view and from its properties is the delta phase of plutonium with cubic crystal lattice (fcc). Let's observe just some of the «peculiarities» in the delta phase behavior:

- crystal lattice stabilization by a low number of alloying elements (1-3 at.%), with lower and higher atomic volume;
- anomally low density;

increase of delta phase density at the rise of temperature (fig. 17); etc. [21, 22].

Plutonium atoms easily change their electron configurations and size when their surrounding in the lattice changes. For example, energy levels of 6d and 5f orbitales are at close range, electron configurations $5f^67s^2$ and $5f^56d7s^2$ compete with each other. Thus, many fundamental plutonium properties depend on 5f electrons, their change from drifting to localization. The reason for such transfers is still unknown.

There are many half-empirical approaches to the unusual behavior of plutonium. One of them even views the mixing entropy of two node types as one of influencing factors, causing the constant thermal transfer from α-phase to δ-phase [23-26]. However, there is no physical interpretation for this hypothesis.

Also there is a sensitivity of plutonium to perturbations, especially to the disorder [27] that we can directly link to the increase of mixing entropy basing on our considered approaches. This was shown in magnetic moments appearing in self-inflicted damage from α-decay of plutonium. The most interesting is their disappearance in thermal annealing. In our opinion, this point out not only healing up of damage at annealing, but the different disorder state at various temperatures in a specific phase, i.e. the possibility of *mixing entropy changing from temperature.* This feature had not been found in the other systems.

Let's try to explain the plutonium behaviour from the position of thermodynamic approach, outlined in the previous chapters, by expanding its interpretation of the energy meaning of configurational entropy.

Phase stability of every alloy depends on the free energy – the sum of internal energy (ΔH) and entropy part (TΔS). Let's get back to the classic Boltzmann definition of entropy as a probability of system states, independent from how these states are defined: by unlike atoms, as it is usually treated in traditional thermodynamics, or other factors. For example, Cottrell regarded electron states entropy as a *type of configuration entropy* [28]. Therefore, our approach to understanding the anomalous properties of plutonium can be summarized as follows [4]:

1. Plutonium should be considered not as a separate element, but as a multicomponent alloy, with plutonium serving as separate components in various electron and phonon states. As a result, the contribution of mixing entropy to the phase properties, stability and transformations increases.

2. Unlike common alloys, entropy factor (mixing entropy) changes along with the temperature and the correlating Debye temperature, causing the delta phase crystal lattice compression at heating and other unexpected properties of Pu.

Let's review these two determininging thermodynamic factors.

1. Plutonium as a pseudo-complex alloy.

Let's look at the aggregate factors that can cause plutonium to become a pseudo-complex mixture: microstructural, electron configurations, temperature, pressure and energy states of atoms and electrons, i.e. atoms with different properties, that can turn plutonium into the state of pseudo-multicomponent solution. Therefore its phase state stability is determined mainly by the entropy part of the free energy equation.

1. Aforementioned orto- and para- nodes of plutonium in various combinations, studied by Cooper [23-26].

2. A multiplicity of electron states with similar energy – additional expansion of valent electron levels.

3. Vibrational entropy. Plutonium mostly has low-frequency oscillations, pointing at the high number of phonons per one mode and, therefore, higher entropy [29].

4. Splitting in the degenerated levels of the valent electrons – as a result, for many of them, the energy does not decrease, for some it even increases, changing the bond strength between atoms and making an additional contribution to disorder and hence, to entropy.

5. Different (harmonic and inharmonic) mode oscillations.

6. Bond hybridization and other fluctuations

The additional proof of the high-entropy state in plutonium is its very high heat capacity, higher for the delta phase (fig. 18) [29-31].

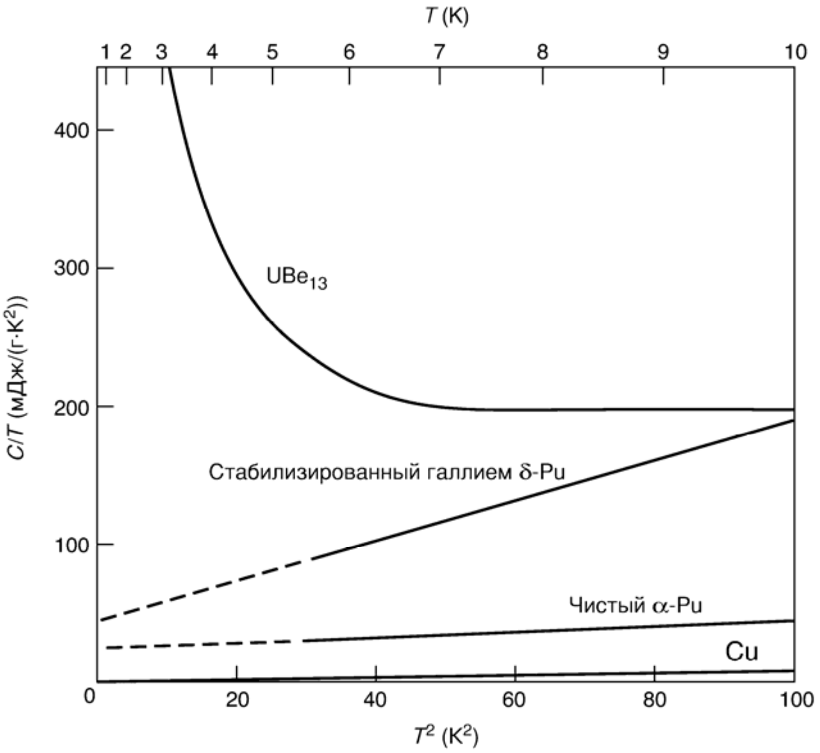


Fig. 18. Specific heat capacity of plutonium and other metals [29-31]

Therefore, plutonium atoms have many possible states influencing entropy. Nominally, it can be classified as *a high-entropy alloy,* with a high contribution by the entropy part. Configurational entropy in some form exists in all plutonium modifications, influencing its phase transformations and physical properties. Furthermore, it can change at heating even in the constraints of a single phase, like in the delta phase, causing anomalous properties of plutonium.

But here we don't have an atomic mixture, but a **pseudomix** of heterogeneous elements, for which an entropy criteria of Boltzmann's disorder **$S=klnW$** could be applied, and its energy contribution could be determined by the second law of thermodynamics. But it should be considered, that the disorder measure can't be taken directly, like in the mixing entropy formula for several atoms **$S=R\sum X_i lnX_i$.** This should not be done, because it is still unknown, how does *the known disorder created by alloyed atoms energetically differ from the neglected disorder introduced by the other factors, particularly, the electron structure.* Additionally, in the latter case, not all node placements with different electron state (mode) of Pu atoms are going to be equal. Plus, some clustery is possible. As a result, the configuration entropy value would be significantly lower. Thus, a correctional coefficient **v** (depending on each energy contribution) should be introduced to the formula and it will always be less than one.

.

$$S= vklnW = vR\sum X_i lnX_i \, . \qquad (23)$$

2. Configurational entropy change depending on the temperature.

Configurational entropy is a comprising part of common entropy, as shown in chapters 7 and 8 [1], can also be expressed through the oscillation energy of the atoms and, therefore, the heat capacity. The common heat capacity graph is presented on fig. 19 a. As seen from it, there are no heat capacity value gaps within the bounds of a single phase, and the Debye temperature remains constant, independent from the temperature.

We observed change of Debye temperature (its decrease) only when the components mixed [1].

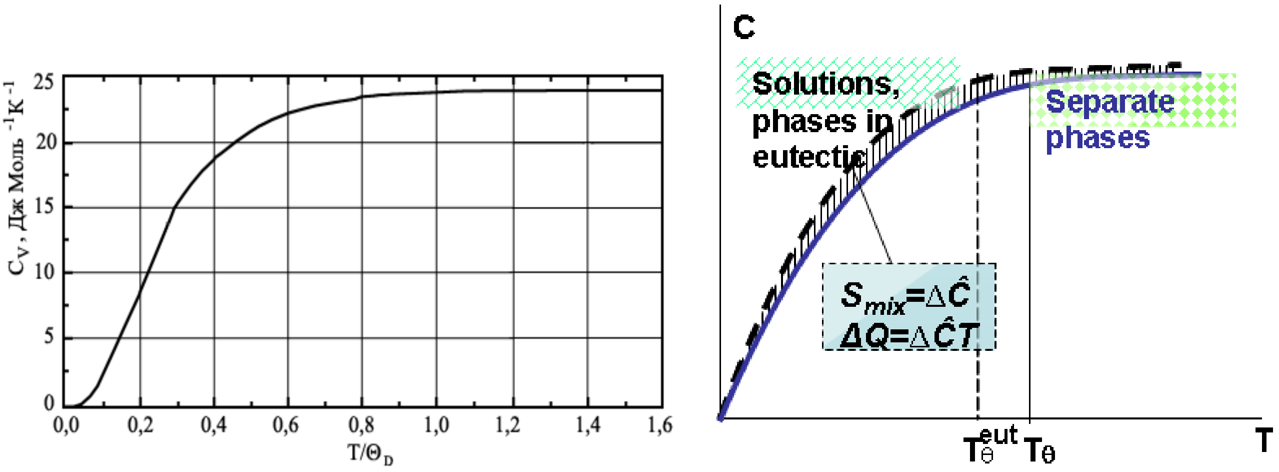


Fig. 19. Heat capacity $C_v(T)$ *dependence, calculated in the Debye model. X-line is reduced temperature* T/Θ (a), *the change of specific heat capacity at ideal mixing, solid curve – original isolated phases (average reduced values), dotted curve – solid solution (b) [1-3]*

But for plutonium, in alpha phase and it is more important in delta phases the change of Debye temperature occurs at heating (fig. 20) [32, 33], as determined by the softening of elastic oscillation mode.

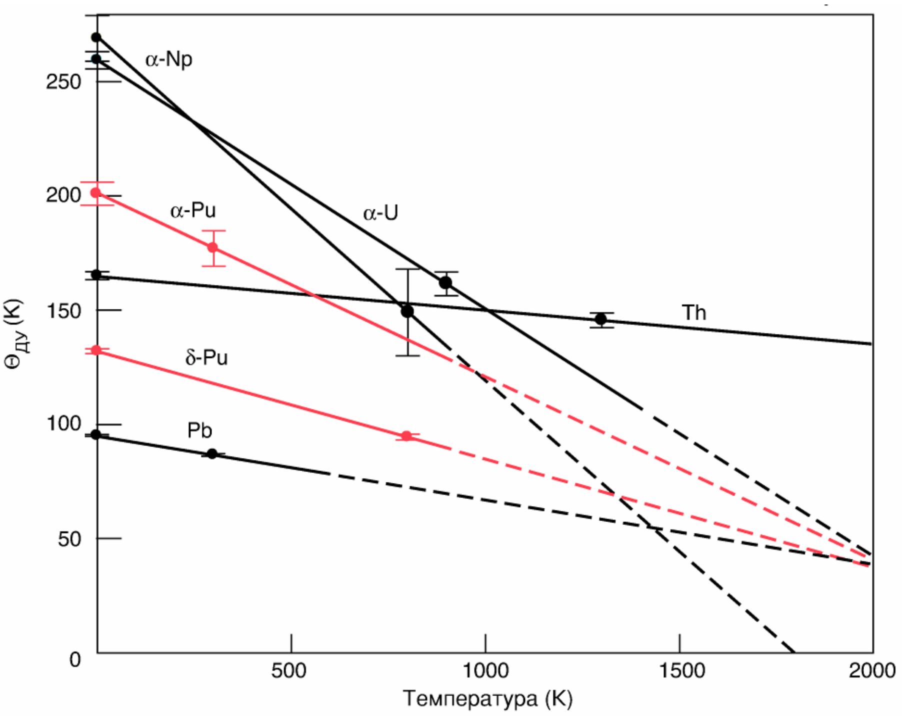


Fig. 20. Dependence of Debye temperature change versus temperature for light actinides [32, 33].

This can be explained only one way – at heating, despite only plutonium atoms being present in the structure, the mixing entropy changes and, therefore, physical properties of Pu change as well. It can cause an unusual change of delta phase properties at heating, as we explain further.

Now, let's see, how this helps to explain some unusual properties of plutonium:

1. Delta phase lattice compression at heating.

2. Long-time stability of this phase, supported at the room temperature by introducing only a few atomic percent of alloying elements into plutonium.

3. Presence of a double C-curve of delta phase decomposition on the TTT diagrams.

1. In all alloys heat expansion always correlates with the increase of specific heat capacity. It has a simple explanation. Energy always increases at heating, along with the amplitude of atomic oscillations. This, in its turn, increases the specific heat capacity and expands the crystal lattice, hence, increasing the thermal expansion ratio. This is not the case for plutonium in delta phase. At heating, naturally, the specific heat capacity increases, but the crystal lattice compresses. In other words, the oscillation energy increases, but the linear expansion ratio decreases. Therefore, instead of the interatomic bond weakening, which is expected when the temperature increases, the strengthening is evident.

Although we have already observed this effect, as described in chapter 8.2. [10]. Then the strengthening of interatomic bonds occurred just like with high-entropy alloys (see ch. 11), at the increase of mixing entropy. Does the mixing entropy increase occur in our case?

The criterion for mixing entropy increase is the decrease in Debye temperature (fig. 20). Precisely this happens with the delta phase. In fact, the average heat capacity increases and, as a result, the interatomic bond strengthens. As a result, the delta phase lattice parameter decreases and its density during heating increases.

2. At the moment, the stability of fcc cubic δ-phase of plutonium is not fully understood. Therefore, there are still questions regarding the long-time stability of that phase, that can be preserved at room temperature by introducing just a few atomic % of gallium into plutonium [17, 20].

But, as we have already shown, the plutonium atoms should be viewed as a pseudomixture of various elements, and not as atoms of the same nature. These elements should be subject to the application of the Boltzmann’s entropy disorder criteria **S=klnW** and calculation of its energy contribution with the second law. In that case even a small additional mixing entropy contribution of alloying elements, independent of their atomic radius, can significantly increase the disorder of electron structures and the mixing entropy increases.

3. Isothermal phase transformation δ→α’, unlike the common transformations, can have kinetics, described by the «double S-curve» on the time-temperature-transformation diagram (TTT), presented on fig. 21 [34]. This means that the δ→α’ transformation has two temperatures, with maximum transformation speed, while there is only one temperature for most martensite transformations.

However, the delta phase of plutonium could be viewed as a solid mixture of several “pseudo” components with varying electron states, additionally changing with temperature. Thus, the decomposion of a solid solution could be viewed as a mixture of two solid solutions with different mixing entropy and, therefore, with various stability. Naturally, they would decompose at different temperatures.

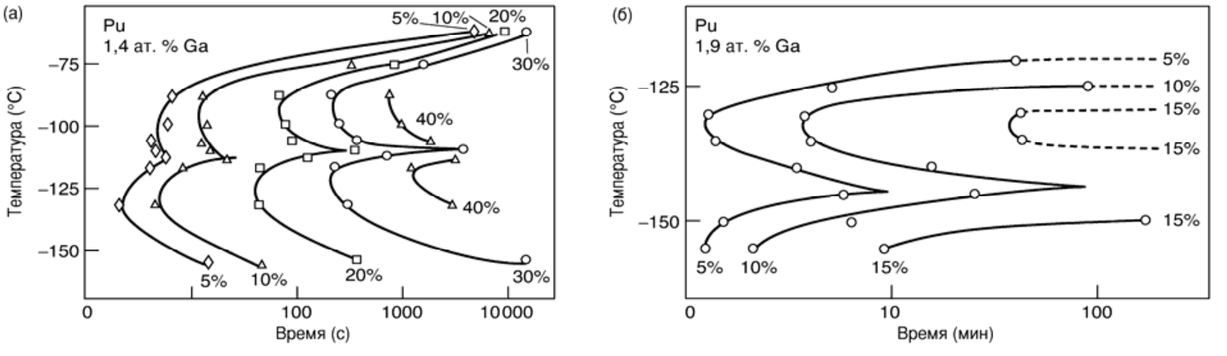


Fig. 21. TTT graphs of δ→α transformation. This diagram showcases the unusual kinetics described by the double S-curve, with two temperatures (-132^{0}C and -155^{0}C) at the maximum transformation speed [34]

14. Qutb column in Delhi. Creation methods for corrosive-resistant non-rusting iron.

Iron and its carbon alloy, - carbon steel – is still the most widespread construction material, mainly due to their low cost. But the iron resistance to corrosion as for most bcc lattice alloys is fairly low, which limits the service life of iron structures or requires an additional protective surface or alloying [35-37]. For example, the Eiffel Tower is painted over annually – its cost has already exceeded the cost of construction. But there is some data on iron construction that are not affected by rust, despite no difference in composition. For example, the Qutb, or Maharsulu column in Delhi [38]. Its height is 7.2 m, weight – around 6.5 t (fig. 22). Over the last thousand and half years, there is not rust on it, and even a tiny Sanskrit scripture can be easily read.

Fig. 22. The Qutb column in Delhi [38]

The origin of this column and the technique used to create it are unknown, but it is presumed, that it is created from meteorite iron. Its composition is not different from usual technical iron - 99,7% iron, 0,1% phosphorus, the rest – sulfur and carbon additives.

Naturally, modern scientists tried to find out the secret of that column to replicate the technique, some difference in its properties and structure, in order to replicate this wonder in industrial condition, but haven't found out any major difference. There is no principal difference in the structure or composition of the non-rusting iron. There are tens of workgroups around the world dedicated to these studies. The research continues.

The fact that the scientists failed to discover any differences points out the necessary direction. The answer can be found where the traditional metal physics and thermodynamics of alloys due to their incomplete knowledge are powerless – in the energy influence of mixing entropy.

Iron, just like the aforementioned actinides, is a transitional metal, which internal d-electron levels are overlapped by external ones due to the similar energy levels.. Therefore, a multiplicity of electron states with similar energy can occur, leading to the additional expansion of electron levels. Also, the iron is ferromagnetic, the d-electrons covers have parallel spins. But as the temperature rises to the Curie point, the part of electron pairs of opposite spins increases. This process causes the increase of mixing entropy, reflecting on the increase of heat capacity and, as we have shown earlier, strengthens the interatomic bonds and the chemical inertia of the material. The high value of entropic energy shows the phase change from ferromagnetic to paramagnetic state above Curie point (768 degrees). Even while this change is a phase transformation of the first type (i.e. occurs in the temperature range without changing the metal phase structure), hidden energy processes occur during it.

In the changing area to the right and to the left of it in the 400 degrees range we observe a sudden increase of iron heat capacity (almost 3 times) peaking in the transfer point (fig. 23.) [39].

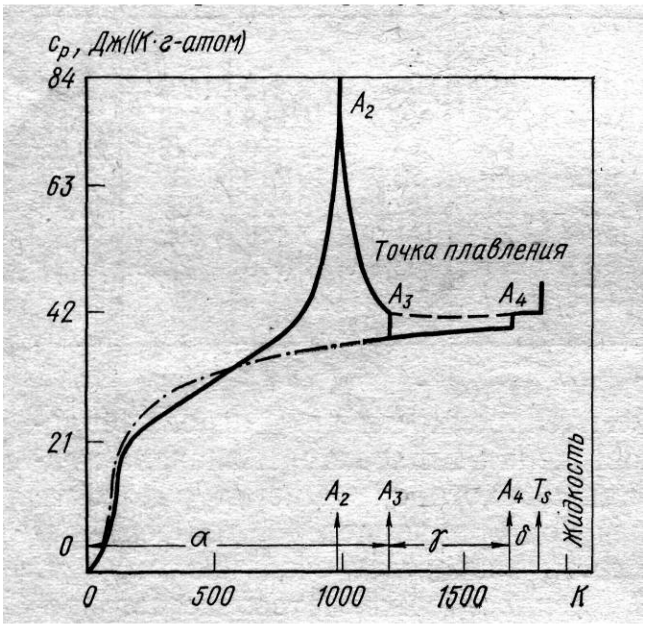


Fig. 23. Atomic heat capacity change in heating iron [39]

The area under the heat capacity curve in the heat capacity–temperature coordinates is equal to C*T and corresponds to the heating energy. If we calculate the space under the heat capacity curve, it would be 150 kilojoules/kg or 3 kilojoules/mole. So, the energy excess is 3 times higher than the phase change from **α-Fe** to γ-Fe (1,0 kilojoules/mole), and only 4,5 times lower than the melting enthalpy of iron (13,8 kilojoules/mole).

Despite the fact that in the phase transition of the first type the energy is not released, the change in heat capacity is equal to the hidden energy emission (at cooling) or the hidden energy absoption (at heating), which is latent and masked by the heat capacity increase.

Therefore, in order to increase the chemical inertia, the interatomic bonds should be strengthened. This may be achieved by the increase of configurational entropy due to the increase in a number of various electron states of iron, especially through the d-electrons, transforming them into a mixture of para-ferromagnetic state.

We have done a series of preliminary experiments, where iron samples were affected by a complex electromagnetic and thermal treatment. Standard 80 mm steel nails were used as original samples (fig. 24 a). Their external view before and after tests is presented on fig. 24 [2, 40].

a b

Fig. 24. External view of original samples before (a) and after a complex electromagnetic and thermal treatment (b) [2, 40]

Unfortunately, the available equipment was insufficient to reach the planned treatment corrosive resistance parameters. Nevertheless, even such treatment caused significant change in properties.

After the treatment, samples became somewhat grey. Some time after removing this film, it appeared again, while the original samples remained unchanged, aside from rust patches.

Corrosion tests had two modes.

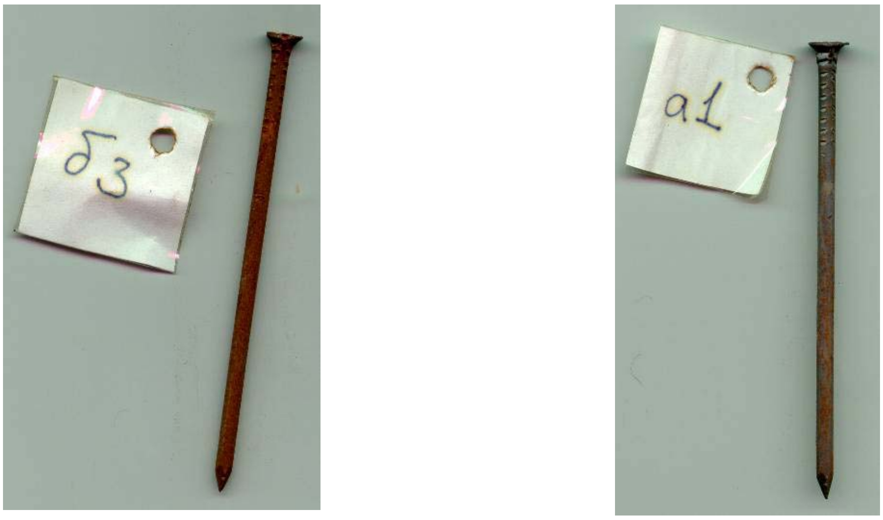
In the first case, the samples were tested in the atmosphere conditions at 10-30^{0}C temperature for a year. In the second case, the intense, short tests were done at temperatures from -20 to +60^{0}C and humidity from 20 to 100%.

In long atmosphere tests the treated samples almost did not change their outlook (fig. 25b). At the same time, the original samples corroded a lot [2, 40].

a b

Fig. 25. Exterior of the samples after atmospheric tests, a – original samples; b – treated samples [2, 40]

The difference is less evident in intensive corrosion tests (fig. 26). Corrosion occurred in the treated and non-treated samples. Should be noted, that the corrosion of treated samples, calculated from the oxide film weight, was around two times less [2, 40].



a b

Fig. 26. Samples exterior after short, intensive tests, a – original samples; b – treated samples [2, 40]

These studies were paused due to the lack of interest and financing. Nevertheless, in our opinion, this direction – to increase a corrosion resistance by increasing the configurational entropy - is very promising. As we have noted, [1-4] Cottrell viewed the electron states entropy as a type of configuration entropy.

Should be noted, that despite the stopped tests, in the span of last 13 years, at temperatures from 10 to 45 degrees, the treated nails have not changed, but the non-treated ones completely rusted.

15. Heat pump based on the osmotic pressure – "perpetual mobile" of the second type?

In the previous article (ch. 5) [1] we considered osmotic processes as one of the proofs of the energy nature of statistical entropy (mixing entropy). We noted, that in mixing, two diametrically opposite processes occur – energy emission due to strengthening of interatomic bonds and energy absorption due to the increase of average heat capacity [2, 3]. If we try to **separate** these two processes in time, like it happens during osmosis, we get the Heat pump based on osmotic pressure - the "perpetual mobile" of the second type.

At the usual mixing of components, we don't see any effects, because they are hidden. But if we do this through a half-penetrable membrane that allows only solvent molecules to pass, an osmosis occurs — the one-sided diffusion process of solvent molecules transfer to the side of higher concentration of dissolved matter (lower solvent concentration). Due to the striving of molecules to spread along the whole volume, an osmotic pressure occurs (fig. 27) [41]. The strength of this pressure is high, it can reach 20 atmospheres in the mixture of see and fresh water.

Naturally, this process is used in the field of alternative energy, particularly in the ***osmotic power plant in Norway [42].***

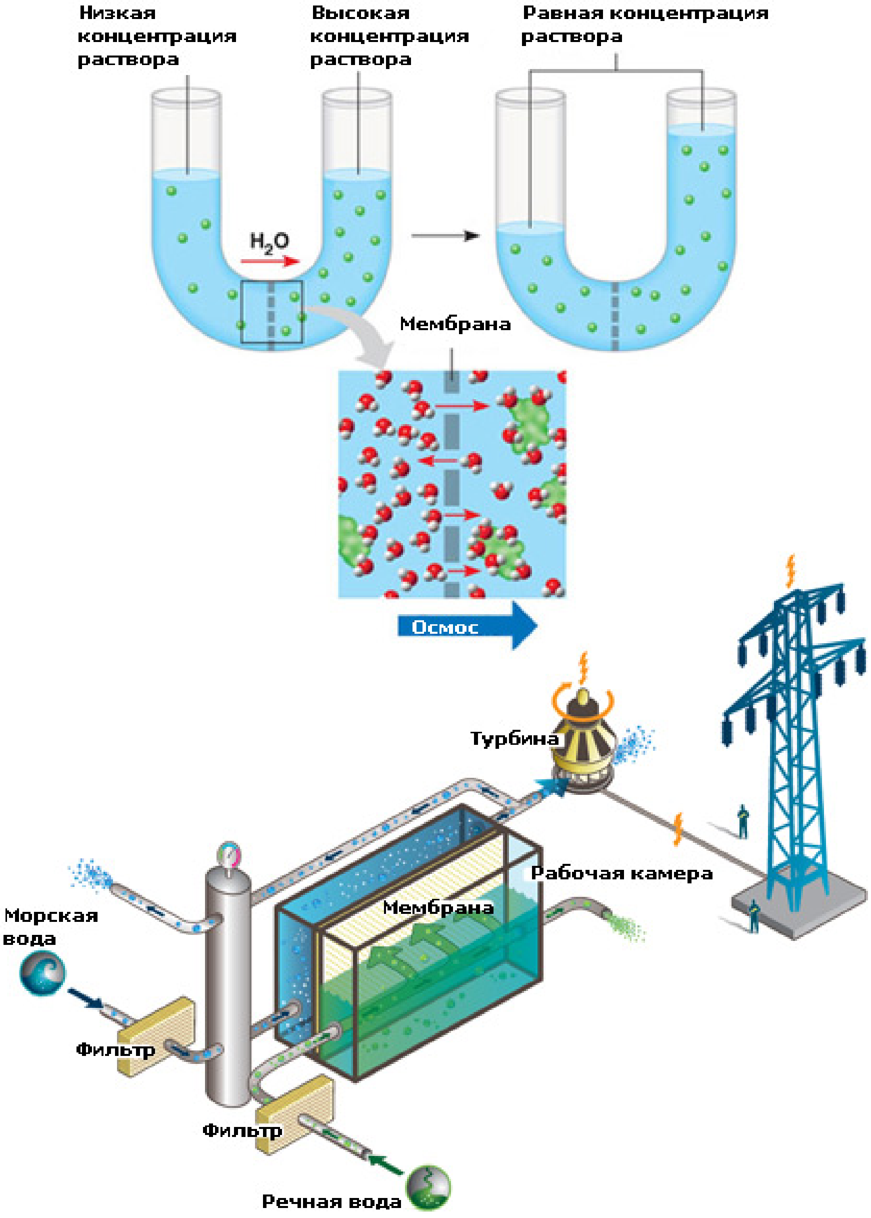


Fig. 27. Water transfer through a half-penetrable membrane and the usage of mixing process in osmotic power plants [41, 42]

The process can be locked by using the reverse osmosis, with salt and fresh water separated (fig. 28) [2]. Membrane at one side and nothing at another. Despite the low pressure in reverse osmosis, it would still occur due to the difference in concentration in the sides of membrane. There are some *solutions*, in which the reverse osmosis occurs easily, which is important for a closed system.

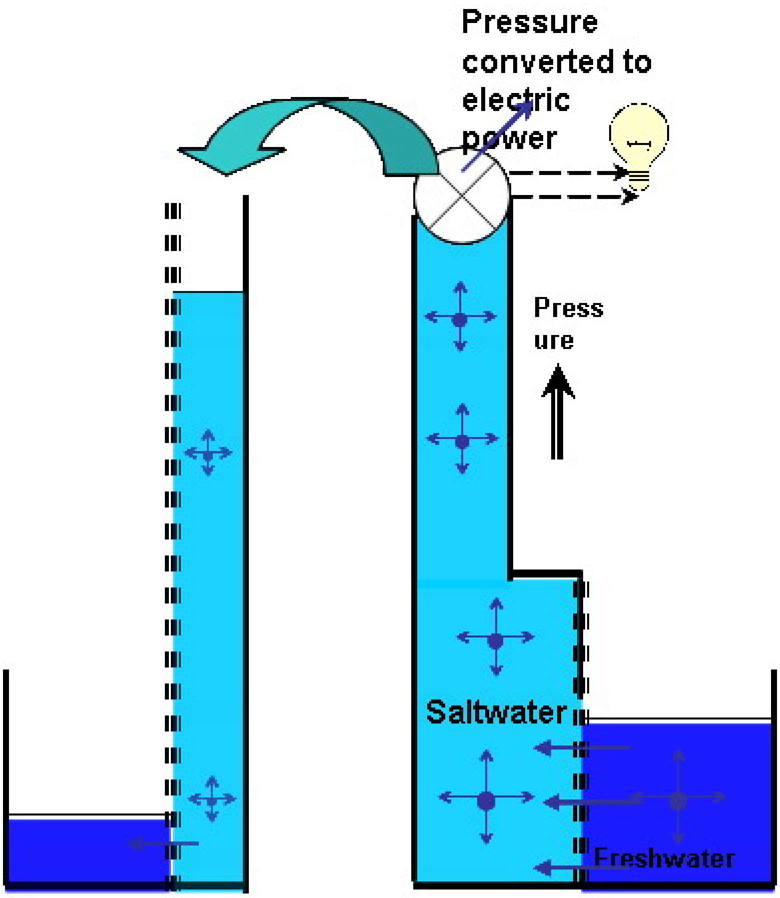


Fig. 28. Reverse osmosis scheme (closed cycle) for generating energy [2]

Therefore, it turns out to be some kind of perpetual motion machine of the second type, if we take pressure energy from direct osmosis we could close the process by separating salt and fresh water. The work of such system would not violate the first law of thermodynamics because the water temperature would decreases. But how does it work in regards to the second law of thermodynamics, prohibiting the energy generation without a temperature difference? In this case, it can be passed by equating the system with a heat pump, which works without violating the second law, if the traditional thermodynamics is to be believed. Even while the heat pump produces 5-10 times more energy than it wastes on the cold agent circulation, it was not possible to close the cycle due to the low temperature difference created by the pump. In case of osmotic heat pump, the created feature could be considered a useful work spent to support the system circulation. Hence, there is a difference between a heat pump and an osmotic pressure pump.

The traditional heat pump creates a lowly effective heat, that would be difficult to transform into electic energy and thus, its work does not bother the acolytes of the traditional thermodynamics. In our case the osmotic heat pump creates electric energy more than energy spent on circulation – such scheme could cause political difficulties from traditional thermodynamics.

How does a heat osmotic pump work?

Let's review several variants, all based on the main principle – increase of water molecules energy at mixing (fig. 29 a).

The forming pressure creates equilibrium in an osmotic process. There is a work done on the water solution due to the mixing entropy. Without the membrane, all work is spent on increasing the average heat capacity and is absorbed by the water solution.

In osmotic processes, the pressure opposes the increase of average heat capacity. Therefore, in osmosis the work is spent to increase pressure (increase the molecules energy), which impedes the increase of average heat capacity and even causes it to decrease. It is known that the specific heat capacity of water slightly decreases with the increase in pressure [45].

But in energy sense, this miniscule difference is sensitive, because it is multiplied by the temperature of the process T ($\Delta E = \Delta CT$). Therefore, there is mixing going on, but due to the pressure the system cannot produce work to increase the average heat capacity (fig. 29 b).

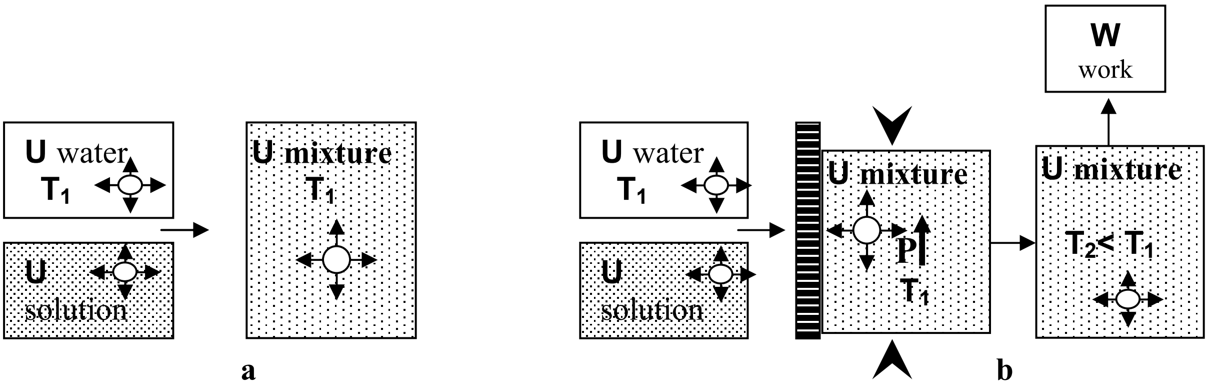


Fig. 29. Mixing processes scheme without (a), and with (b) a half-penetratable membrane. In the latter case, the energy emission and the increase of average heat capacity are separated in time, which allows to use the mixing energy.

When the osmotic pressure is turned into useful work – electric turbine rotation – there finally appears a balanced process of the average heat capacity increase in the solution. But the molecules energy has already become smaller due to the decreased pressure. Therefore, the energy for heat capacity increase is taken from the cooling of water.

Hydraulics researchers have noted, that during the water pressure increase **P** a work **$dE=VdP$** is being done over it, despite next to no change in the volume of water **V** [45, 46]. This complies with the law of energy conservation – the pressure work should go somewhere.

It is known, that the pressure is energy, characterizing the atomic and molecular oscillations, their movement speed for gases and liquid, the amplitude and frequency for liquids and solid bodies. In case of osmosis, a higher concentration of water molecules is compensated by the higher oscillation energy by pressure increase from the other side of membrane. When the water pressure is used to do useful work, the water molecules energy would naturally decrease and the water would cool down. Then, by heating up, the separated components of the mixture get into the system again. The cycle continues.

Therefore, this osmotic pressure system works as a heat pump, taking heat from the water and transforming it into useful work – energy generation without violating the thermodynamic laws, even while there is no initial difference in temperatures of fresh and salt water. There are other conditions. Molecules have different speed and energy, which is always present in nature, according to the Maxwell-Bolzmann distribution. But the main thing is that they are separated by the half-penetratable membrane, allowing to realize the «Maxwell's demon» principle.

It looks like there could be other methods to use the atomic oscillation energy at usual temperature without creating a temperature difference. This does not directly violate the second law, because the fluctuations of oscillations can always appear. It is most clearly expressed in the mixing processes due to the dynamic process of increase in atomic oscillation energy and the appearance of different energy fluctuations is most likely.

16. **Reverse transformation of vibration entropy into configurational one and its consequences**

In the previous article [1] we have shown, that mixing entropy (statistical entropy) has an energy context and can be expressed through the heat oscillations of atoms. Nominally, statistical entropy is equal to vibration one and in mixing it causes the increase of the latter (transfers into it). But is the reverse transfer possible – is there a reverse connection? Can the vibration entropy be expressed through a possibility of states (statistical or mixing entropy)?

In order for various states to exist, there should be conditions for the difference in the energy of atomic oscillations. It already exists in nature, if we look at the statistical distribution of molecules by speed (Maxwell-Bolzmann) (fig. 30) The nominal quantization by molecule speed value expressed by helium molecules on the graph, could be explained as a statistical distribution, i.e. the statistical entropy. Thus, the vibration energy of molecules at the current temperature could be viewed as a statistical one (configurational entropy).

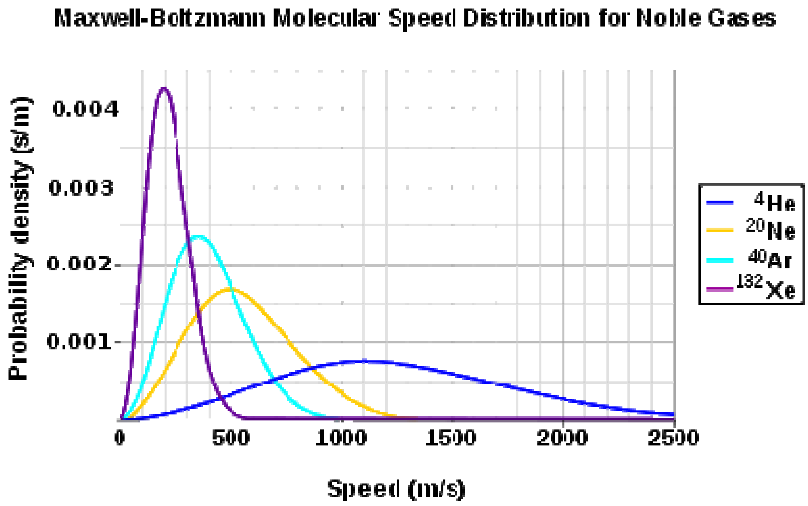
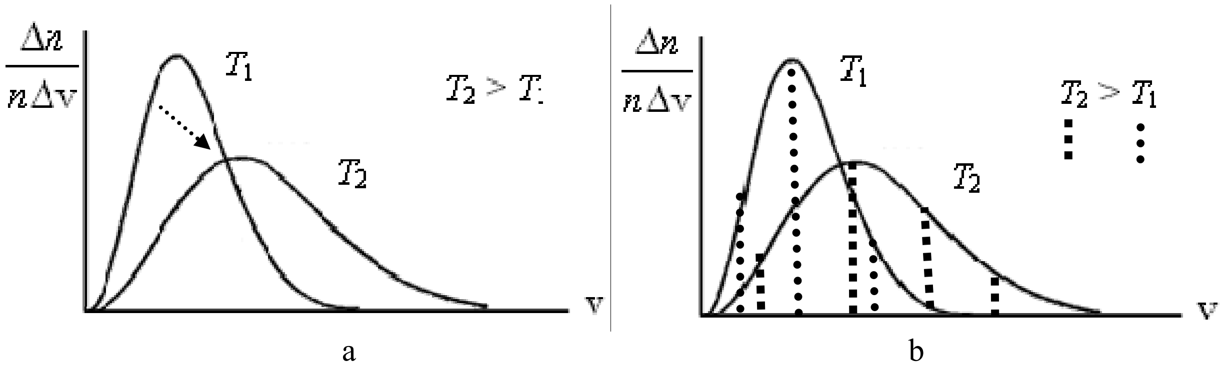


Fig. 30. Statistical distribution of molecules by speed (Maxwell-Bolzmann) for inert gases helium (^{4}He), neon (^{20}Ne), argon (^{40}Ar) and xenon (^{132}Xe) at 298 K (change in molecule speed depends from mass)

Even clearer this connection appears to be in the increase of temperature. Increase in vibration entropy with temperature increase could be connected with the increase in number of additional energy states, caused by the higher energy oscillations of atoms. This is seen on fig. 31 a, with the statistical distribution of molecules by speed (Maxwell-Bolzmann) for one type of molecules versus temperature. It is seen, that along with the increase in temperature there is an increase in number of molecule states with various speed and energies, i.e. the chaos in their distibution increases. If some nominal quantization is introduced (fig 31 b), it would be possible to mathematically express the vibration entropy through the configurational one.



a

b

Fig. 31. Statistical distribution of molecules by speed (Maxwell-Bolzmann) by temperature at 298 K (a); (molecule speed change depends on temperature – degeneration (splitting) at temperature increase); (b) nominal quantization of energy states

Therefore, a reverse connection could be seen too and its possible to express vibration entropy through the mixing (statistical) entropy. Maybe it is a way to solve the Hibbs paradox.

17. The possibility of molecules heat energy use without a violation of the second law of thermodynamics. Are there other limitations?

Naturally, a question arises – if there is such variety in molecular energy even at room temperature, could this process be used practically to realize the long forgotten Maxwell's demon on a higher, modern level of science? We have shown, that this is possible for osmotic processes, but it is a particular case, and the energy there is not generated in a "pure" way, but with the use of mixing processes.

There are natural processes violating the second law. The basis for these processes lies in the two main natural properties of matter. Firstly, even at the room temperature, gas molecules have enormous energy, their speed reaches hundreds of m/sec. However, their movement is chaotic and spread over all three dimensions (Brownian motion). Secondly, their distribution by speed is unequal, described by Maxwell formula, and changes from tens to hundreds of m/sec at current temperature. With that, for some reason, the molecular energy does not average out (natural law). Therefore, the nature leaves us at least three ways to create a "perpetual mobile" of the second type at constant temperature:

1. Molecule separation by speed. Water evaporation from a porous jug – water molecules with higher energy (speed) fly out from the surface, molecules with lower energy remain in the water, cooling it. Thereforem there is a natural separation of hot and cold molecules and the creation of a temperature gradient.
2. Molecule separation by speed and direction. When whirlpools and vortex form, there is a natural molecular distribution by speed in their bodies. In addition to that, molecule vibrations transform chaotically in three dimensions, mostly directed along with the twist. Then, after whirlwind produces work – it increases due to new portions of air being sucked in – it loses the kinetic energy, destroys itself, and air molecules become chaotic again, with lower energy. As a result, the air temperature lowers. The formation of whirlwinds (tornado) is always accompanied by the decrease of temperature.
3. Molecule separation by direction. These effects appear in occurrences like hydrostrike and acceleration laminar stream of gases and liquids. It obstructs the vibrations on two directions and eases them up on the main direction. As a result, the liquid pressure increases, it can be transformed into useful work. After energy loss, the liquid cools down in accordance with the first law of thermodynamics.

The absolutization of the second law is reflected in the E.G. Oparin's «Physical laws of fuelless energy (the limits of the second law of thermodynamics)» [46]. He showed that there is still a confusion in regards to the usage and invariance of the second law of thermodynamics (free energy decrease). Originally, the second law was only formulated for an ideal heat machine with ideal gas. Later, Clausius, Thompson and other scientists expanded its application to the whole Universe, proposing a Universe heat death hypothesis. Then, the process of the second law application reversed. At first, the absurdity of the heat death of the Universe, i.e. it inapplicability to the micro world (quantum mechanics), was proven. One of the founders of the second law himself, Thompson, pointed out the inapplicability in case of "plant growth or similar chemical action".

Should be added, that astrophysicist Nikolai Kozyrev has experimentally proven that any entropy process causes and is accompanied by an anti-entropy process [47, 48]. In this case Lentz rool can be implemented [3].

Oparin makes some examples of working perpetural motion engines of the second type – F.M. Lazarev's colzar [49], thermophase engine of A.I. Weinick [50, 51], E.G. Smenkovsky's molecular reactor [52, 53] etc. All of them are based on the liquid evaporation and condensation effect – their circulation through the microporous membrane.

It is fair to say, that these effects are small and there still has not been a pilot installation with a significant energy effect on output.

We don't look at the effects affecting the molecular distribution alongside the direction, it will be examined further, along with the antistocks luminiscence effect in luminosphores – both of them are realized during the molecular movement transformation into mechanical work trough the environment cooling off.

Non-equality of molecules distribution by speed and energy is a hidden restriction of the second law of thermodynamics.

Naturally, a question arises – why all this enormous energy is not put to use, what are other, yet unknown restrictions? The scientific, not administrative ones – not the Academy of Sciences bans and the like.

To create such heat pump it is necessary for molecular dispersion by speed to be identical to its dispersion by energy – because we intend to use the energy difference. It applies in the traditional approach; the graphs align with each other. The moving molecules energy is defined by kinetic energy and is equal to $mv^2/2$, its unequal distribution lets take excessive energy from the nature. But is it true?

It is known, that the complete energy of the molecules or atoms is equal to the sum of kinetic and potential energies $E_\Sigma = E_K + E_П$. Let's look at a single oscillator, emitting energy $h\nu$. It works as a retranslator, takes energy from environmental temperature T and is connected by the well-known formula:

$$E = h\nu = 3/2kT, \qquad (24)$$

where k is a Boltzmann constant

But oscillations represent the transfer of potential energy into the kinetic one and in reverse. There is no internal source for an oscillator. If it starts the Brownian motion, it need to get kinetic energy $mv_i^2/2$. And it can only get it from the energy of its own oscillations $h\nu_i$. Therefore, oscillation energy decreases (the frequency lowers). Therefore, the moving source at given temperature has complete energy - kinetic E_K and vibration (oscillation) E_B, taken in different proportions, depending on conditions:

$$E_\Sigma = E_K + E_B = h\nu_i + mv_i^2/2 = 3/2kT = h\nu_o, \qquad (25)$$

With that, $h\nu_i$ and mv_i^2 are naturally less than in a single oscillator ($h\nu_o$). This is kinetic/oscillation ratio and, therefore, the oscillation speed/frequency one can constantly change by time and after molecules push (collide) with each other and with an obstacle (wall). With that their complete energy E_Σ remains constant (fig. 32). Even if molecule (atom) remains in the solid or liquid lattice (pseudo-crystal lattice with short range-order), these proportions somewhat remain. In a crystal lattice the kinetic energy correlates to the energy of atomic deviation from the balance position.

Let's see what happens when molecules push (collide) with each other and a wall.

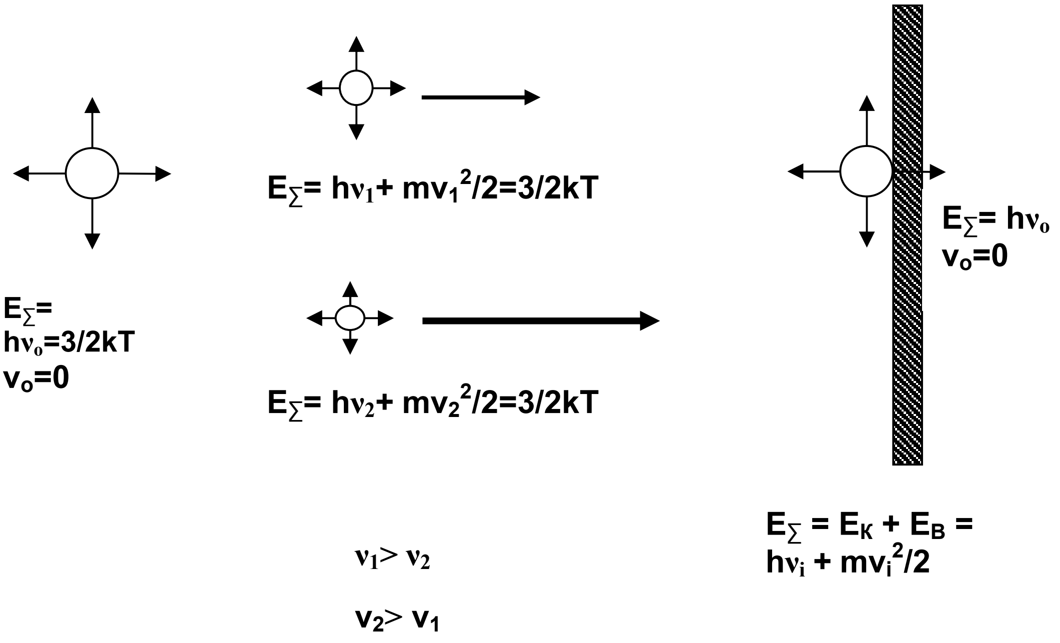


Fig. 32. Scheme of transfer from a single oscillator to a Brownian motion with a proportion change between kinetic energy E_K and vibrational energy E_B.

At the moment of collision, the molecule speed $\mathbf{v_i}$ and its kinetic energy are egual to zero. But its vibration energy is not equal to zero. On the contrary, it rises to the maximum, like in a single oscillator. when then the molecule re-bounces from the wall the energy once again redistributes from vibration to kinetic one.

The wall has same temperature, therefore,it cannot absorb all energy $\mathbf{3/2kT}$ and it is also a subject of energy redistribution.

If two molecules collide, then their complete energy does not change, but the proportion of vibration and kinetic energy can change.

Therefore, it is difficult to extract the excessive energy, despite the fact, that the distribution by speed lets do it in theory. Unlike the experimentally proven molecule distribution by speed (and, therefore, only by kinetic energy), the total (kinetic plus potential) energy difference is minimal.

Of course, trying to extract energy without temperature difference is not that hopeless. Firstly, the statistical mechanic that connects entropy with a probability of a macro system state by a Boltzmann proportion «entropy-probability», also looks at the special process class – fluctuations, during which the system changes from more to less probable states and its entropy decreases. The fluctuations show that the law of entropy increase is only executed in a *statistical way:* at average for a big range. Thus, the molecule distribution by energy is possible, even for a limited context. Secondly, the accelerated movement of gases and liquids can be used when the acceleration overlaps with a chaotically vibrating particles. In this case, molecules get additional energy or, from the energy conservation point of view – temperature. We automatically go by pointer from distribution by speed 1 on fig. 31 to distribution 2. As a result, one molecules press on the other and for a short time to achieve more uniformity in the accelerated molecules and there can be a brief speed acceleration in the direction of forward movement and the prevalence of kinetic energy over vibration energy. This brief moment can be used to get energy. Then, as the movement stabilizes, the temperature would lower down.

Constant molecular acceleration occurs in whirlwinds (vortices) and equal rotational movements, which could be used to generate energy by this mechanism.

We could also use the very moment of molecules striking the membrane, like hydraulic shock, and try, like in osmotic processes, separate the moment of kinetic-vibrational energy transfer and try to use it. We can also add short-timed change from chaotic nature of molecule oscillations to reciprocate (forward) movement at sudden deceleration or acceleration of gases and liquids. But for this we must properly simulated these processes, especially the mechanism of transfer from vibrational to kinetic energy.

Most likely, such mechanisms get realized in the anti-stokes luminescence, with some luminophores redirecting the light with a different, shorter wavelength – and, hence, the higher energy [46]. The addition to energy quantum light occurs due to the transformation of luminophore's own thermal energy into the luminesce emission energy. Luminophore cools down due to thermal energy withdrawal. This effect is used in productions to cool down materials with temperature lower than liquid helium.

Most likely, it occurs when the light frequency oscillations resonate with luminophore's own atomic oscillations. They are summarized, and luminophore emits a higher frequency. And because the surrounding temperature does not change, it is forced to take energy from its own oscillations, i.e., to cool down.

18. **Conclusion**

1. Practical use of novel approaches to alloys theory and thermodynamics based on hidden effects at mixing processes and energy sense of configurational entropy is considered.

2. Explanation is given to unique properties of so-called **high-entropyalloys (HEA)** by additional strengthening of interatomic bonds in mixing (formation of liquid and solid solutions). Ways of improving its properties is shown.

3. New approaches to modify the thermodynamic databases and programs, like CALPHAD (CALculation of PHAse Diagrams) and Thermo-Calc, by including additional thermodynamic data

and formulas, such as the energy of configurational entropy, average hear capacity of phases in isolated state and in contact, the change in Debye temperature during alloy formation, etc is proposed.

4. With the use of energy sense of configurational entropy an attempt is made to explanation of anomalous in actinide systems behavior, particularly plutonium, as configurational entropy changes during heating and microalloying. It is based on two main principals:

4.1. Plutonium should be considered not as a separate element, but as a multicomponent alloy, with plutonium serving as separate components in various electron and phonon states. As a result, the contribution of mixing entropy to the phase properties, stability and transformations increases.

4.2. Unlike common alloys, entropy factor (mixing entropy) changes along with the temperature and the correlating Debye temperature, causing the delta phase crystal lattice compression at heating and other unexpected properties of Pu.

5. An attempt is made to find out the secret of the Qutb column in Delhi made of non-rusting iron. Increasing the mixing entropy of valent electron states by complex electromagnetic and thermal treatment we preliminary received the similar corrosion resistant parameters on nails.

6. Carefully studied the mechanism of osmotic pressure formation based on energy substance of configurational (mixing) entropy. It is shown that if we separate in time the energy release and increase of average heat capacity during mixing processes, heat pump based on the osmotic pressure – “perpetual mobile” of the second type can be created without violating the second law of thermodynamics.

7. Reverse transformation of vibrational entropy into configurational one is considered taken into account the increase of a number of molecules states with various speeds and energies, particularly with the increase in temperature as pseudo-mixing process.

8. Consideration is given to the possibility of molecules heat energy use. It is found the additional limitation to the this process in addition to the limitations of the second law of thermodynamics.

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Part 3. Entropy effects in multiphase systems. Phase diagrams and eutectics melting mechanism

It is the ***thid part*** *of a united article: "Hidden» thermodynamics – rational approach to known facts" published in J. Atomic Strategy, S-Petersburg, in three articles (3 Parts - Russian version):*

1. The discrepancy between the approaches to the second law of thermodynamics and phase equilibrium. Solid and liquid solutions, Issue 109, December 2015, 17-23, *available online* http://chronos.msu.ru/images/rreports/Savchenko/Savchenko_Skrytaya_termodinamika_trezvyy_vzglyad_na_izvestnye_veshchi.pdf
2. Entropy effects in real systems,. Issue 110, January 2016, 14-19, *available online* http://chronos.msu.ru/images/rreports/Savchenko/Savchenko_Entropiynye_effekty_v_realnykh_sistemakh.pdf
3. **Entropy effects in multiphase systems. Phase diagrams and eutectics melting mechanism, Issue 111, February 2016, 28-33**, *available online* http://proatom.ru/modules.php?name=News&file=article&sid=6484

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19. Introduction

This is the third final part of the article on the alloys theory and thermodynamics.

The subject of the third part is multiphase systems and eutectics, comprising, unlike solid solutions, the most of alloys [1, 2]. Also, it looks at the modified description of the phase equilibrium by taking into account hidden energy effects, causing the strengthening of the interatomic bonds, and their influence on physical-mechanical and chemical properties of alloys.

In the first part [1] we, based on the forgotten and incorrectly interpreted states of classical thermodynamics, showed that:

- Statistical (mixing) entropy *is identical to the vibration entropy, has an energy context, expressed through the change in the nature of atomic oscillations, can be expressed also as* ***dQ/dT****, which is proven, in particular, by osmotic processes;*
- *Mixing entropy can do work. Mixing process are hard to observe because they occur inside the system and are accompanied by the increase of average heat capacity due to the decrease of Debye temperature, which, according to Lindemann's rule, lowers down the melting temperature;*
- *Even in an ideal mixing, two hidden (latent) processes go on at the same time and compensate each other. First - the increase of average heat capacity, requiring heat absorption to support the constant temperature. Second - at the same time, latent (hidden) heat emission (release),* $Q = \Delta\hat{C}T$, *or hidden enthalpy increase, through the strengthening of interatomic bonds.*
- *Strengthening process of interatomic bonds during mixing (formation of liquid and solid solutions) influences alloy properties, in particular, the ones of high-entropy alloys, neglected by the traditional thermodynamics.*

Would these regularities (patterns) be realized not only in solid and liquid solutions, but also in multiphase alloys?

Heterogeneous systems are formed out from liquid solutions, where the role of mixing entropy is huge and, as we have shown in the previous articles, affects the alloy properties in solid and liquid solutions. But when the system, as a result of crystallization separates into several phases, how does the mixing entropy express itself, what is its energy sense? Formally, according to the traditional thermodynamics, its value gets closer to zero – statistically, there is no atoms mixing, and the mixture of various, even small-disperse phases, males (brings in) a miniscule contribution to statistical entropy, compared to the mixture of unlike atoms ($\mathbf{S_{mix}=k \cdot lnW}$) [3-6]. On the other hand, there should be some continuity at phase transformations and equilibriums. Indeed, we talk about the hidden emission and absorption effects in solid and liquid solutions revealed in the previous articles [1, 2]. Maybe, they are present, but undetectable due to more simplified mechanistic approach – instead of viewing the multiphase mixture as a unified thermodynamic system, it is considered as a *mechanical mixture of phases*.

If there are no gaps in heat capacity curves at low temperatures, when liquid or solid solution separates into several phases (fig. 33), the energy entropic effects from the first article – increase of average heat capacity and strengthening of interatomic bonds – should remain. Indeed, this preserved additional collective interatomic bond, analogous to the metallic bond in a crystal lattice, can also spread to the nearby crystal if they are mutually oriented [7-10].

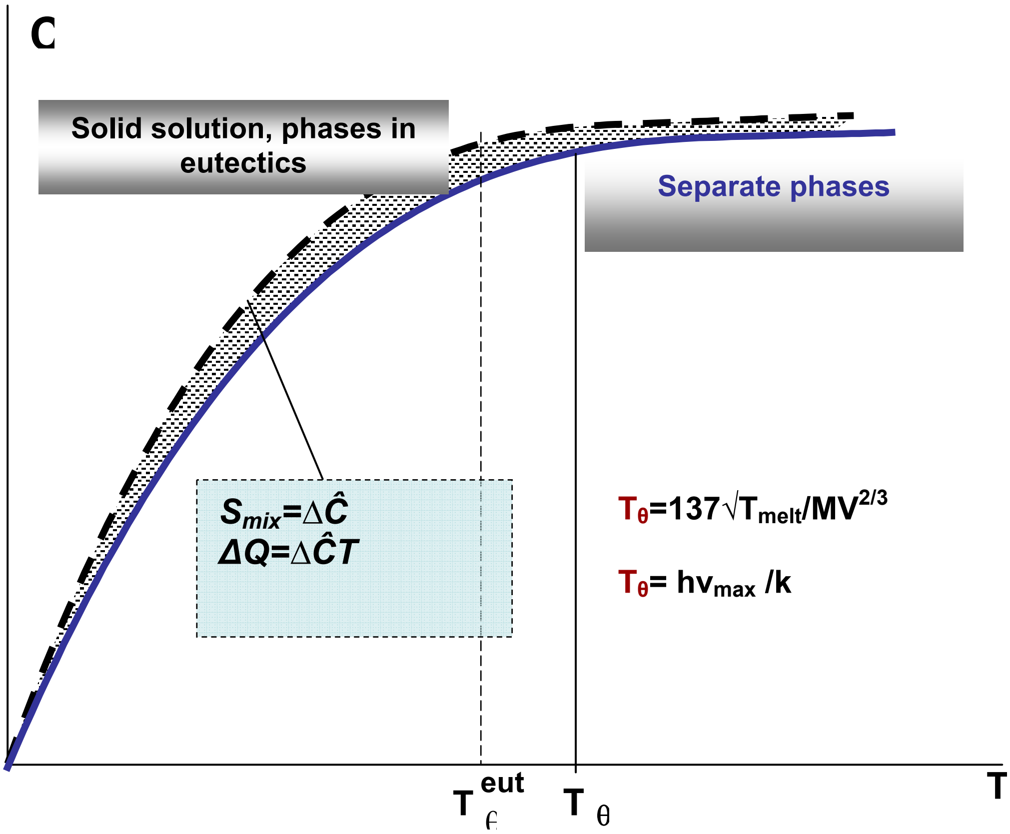


Fig. 33. Specific heat capacity change at mixing (ideal solution). Hibbs free energy characterizes the changes inside the system during mixing. With that, mixing entropy (S_{mix}) and average heat capacity $\hat{C}$ increase. But system does not absorb heat, because the hidden heat emission $Q = \Delta\hat{C}T$ occurs simultaneously. Dotted curve – solid solutions and eutectics, solid curve – original isolated phases (reduced average values) [1, 7-9]

The traditional thermodynamics approach to the phase mixture as a mechanical mixture of phases not only violates experimental data, but also classical thermodynamics, which considers every multi-component system as a unified thermodynamic system. A.A. Bochvar, in particular, in his studies of eutectic alloy crystallization, pointed out the fact of an intricate physical and chemical interaction between phases, that does not take place in a mechanical blend. It points out that the melting temperature of alloys always differentiates from the melting temperature of a mechanical blend: "Eutectics cannot be called a mechanical blend of phases, which is sometimes done. There is no interaction between phases in a mechanical blend. On the contrary, a complicated physical and chemical interaction between phases is observable in the eutectics" [11]. He discovered phenomenon of superplasticity, which expresses itself in a number of eutectic and eutectoid alloys and confirms this approach.

But the *mechanical phase mixture* approach particularly at phase equilibrium description using geometrical thermodynamics method is still widespread in modern thermodynamics*:* it separates the system into isolated components that are then combined by a mechanical mixture principle [3, 4, 12-16]. Thus, the existence concept of an equilibrium phase mixture to be a simple mechanical blend of phases contradicts the second law of thermodynamics since the formation of any equilibrium phase mixture from original components (mechanical blend of phases) has to diminish the free energy of a system and be the major distinction between alloys and mechanical blends. As a result a whole series of phenomena that affects both the properties of alloys and the processes of crystallization and structure formation of alloys were omitted from consideration.

Therefore, while trying to predict the alloy properties, it is mostly the phase content, volume fractions and phase distribution are taken into account, while the presence of an internal interphase bond is ignored. This internal bond forms as a result of mixing entropy energy transformation into the vibrational entropy at crystallization and formation of multiphase system from liquid solution, is a type of interatomic bond, thus it can influence many alloy properties.

20. Analysis of a traditional approach to the thermodynamic description of state diagrams and the discrepancy of multicomponent system phase equilibrium description by geometrical thermodynamics

Equilibrium phase state of any thermodynamic system, including alloys, is determined by the minimal free energy value, for multicomponent alloys – by the free energy of mixing ($\Delta G_m = \Delta H_m - T\Delta S$). Therewith simple U-shaped free energy curves versus composition are constructed of individual isolated phases in an alloy at a specific temperature while the free energy value of an alloy is determined by arrangement of the common tangent line to the free energy curves of the of phases comprising an alloy of isolated phases [3-6].

However, if the thermodynamic description of individual isolated phases available in an alloy and being single phase systems conforms to thermodynamic concepts (separate phase-alloys on fig. 34) then with the description of multiphase systems (alloys) by drawing the common tangent line to the curves of variation in the free energy of isolated phases automatically converts an alloy from a unified thermodynamic system to a mechanical mixture of phases. This means that such a mixture will not melt down at a single temperature, like e. g., eutectics but at melting temperatures of individual phases.

Fig. 34 gives an example of the traditionally phase diagram construction based on the curves of free energy of individual phases versus composition using geometrical thermodynamics method [3, 4, 12-16]. The free energy here is not depending on composition, like in solid solutions, which have parabolic free energy dependence on composition. Therefore, it is not important for a mechanical phase mixture what phase proportions are going to be in alloys **1, 2 and 3**, all of them are on one straight line. Even while there are the same phases, they have different origin – hypoeutectic, eutectic, hypereutectic, and they were formed at different crystallization temperatures, and, therefore, they should have different average heat capacity, entropy and, hence, free energy [3, 4, 12-16].

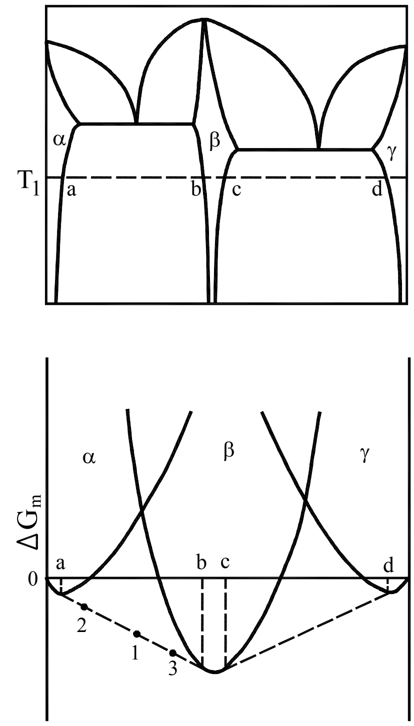


Fig. 34. Free energy of mixing as a function of composition and corresponding to it phase diagram with intermediate phase [3, 4, 12-16]

Another factor of discrepancy in traditional thermodynamics is an impossibility of diffusion processes description. For example, the straight line connecting alloys 2, 1 and 3 on fig. 34, is an equilibrium line between an alloy and eutectic, that have the same phases in their structure, but different volume ratio. Alloys are in thermodynamic equilibrium to each other. In other words, the diffusion processes just like any spontaneous processes leading to the decrease of free energy, should not occur. But if we metallurgically connect alloys **2** and **3**, there would be a composition realignment resulting in alloy **1** with the same phases but in different ratio. Diffusion always causes the *decrease of free energy* in a system. But if alloys are placed on a same line, there shouldn't be a diffusion, because the free energy value of an alloy does not change.

Dehlinger noted that Hibbs' interpretation of a linear dependency would only be correct, if the heat capacity of an alloy does not change, according to Neumann-Kopp rule. But it is not observed, particularly in the eutectic alloys. Aside from that, in contrast to traditional description of phase equilibrium, it also depends on phase proportion, i.e. composition. Otherwise, it only explains a mechanical mixture of phases [17].

Therefore, the accepted traditional description of phase mixture equilibrium (particularly, eutectic alloy) as a simple mechanical mixture of phases contradicts the classical *thermodynamics and* the second law of thermodynamics, because a phase mixture (alloy) formation from original components (mechanical mixture of phases) should lower the free energy of the system, and is the main distinction, between alloys and a mechanical mixture of phases.

21. Transformation of configurational entropy into vibration one at crystallization. The formation of an interphase metallic (entropic) bond at crystallization in multiphase systems

As we noted in the previous article [1], there are two processes occurring simultaneously at mixing and phase formation – strengthening of an interatomic bonds and an increase of average heat capacity due to an increase of atomic oscillation energy, which is accompanied by the decrease of Debay temperature, causing the lowering of a melting temperature according to the Lindemann's rule. This value is different for every alloy and depends on melting temperature. Because alloys always melt in a temperature range, aside from some chemical compounds, that can be referred to a pure components at first approximation), their heat capacity is different, despite the same phase composition

At the alloy crystallization (particularly of eutectic), when the phases split from a liquid homogeneous solution, and mixing entropy formally disappears, in reality, its energy transforms into an increase of atomic oscillation amplitude, i.e. into a common vibrational entropy, increasing the average heat capacity in comparison to the mechanical mixture of phases.

How does it look like from the geometrical thermodynamics point of view?

The phase equilibrium of a multicomponent system in Hibbs' interpretation is determined by a tangent drawn to free energy curves of original phases, comprising the alloy (fig. 35). But the free energy curves could be calculated as applied to the isolated initial phases ($\mathbf{G}_{\alpha+\beta}$), as it is adopted now, or to the phases contacting with each other ($\mathbf{G}_{eut}$), according to the classical thermodynamics.

In the latter case, the free energy curves should be placed lower, because the average heat capacity increases ($\hat{C}_{eut} > \hat{C}_{\alpha+\beta}$). This causes the free energy value of the phases to decrease according to the second law of thermodynamics.

$$\Delta G_{eut} < \Delta G_{\alpha+\beta} \quad \text{since} \quad \hat{C}_{eut} > \hat{C}_{\alpha+\beta}$$

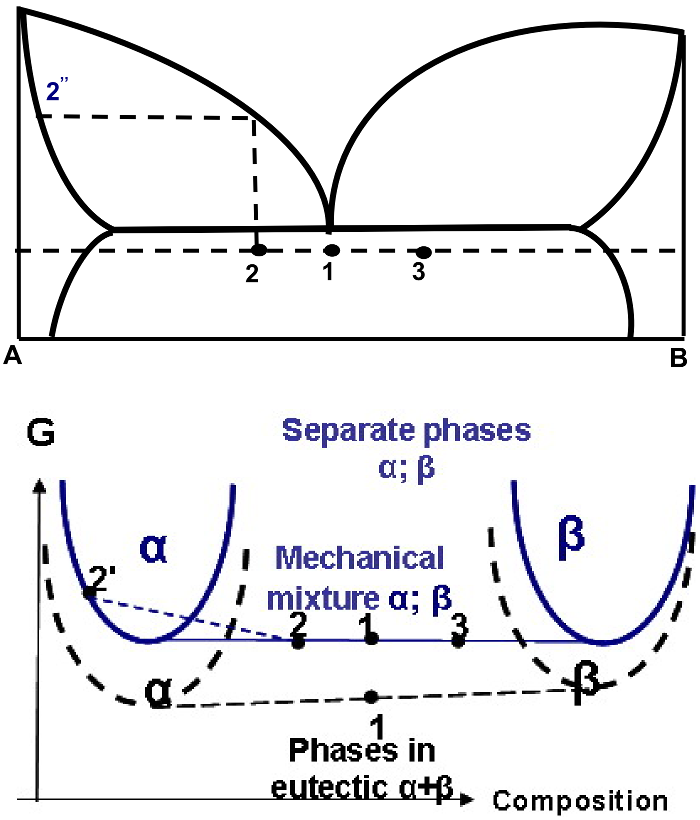


Fig. 35. The description of phase equilibrium in eutectics (free energy of mixing vs composition): *traditional description - (solid blue line – average reduced value) – usage of free isolated phases in an alloy – phase equilibrium does not depend on alloy composition;*

Proposed description according to the classical thermodynamics - (dotted black lines) – usage of free energy from phases contacting with each other – phase equilibrium depends on composition [7, 8]

For example, lets calculate free energy value **ΔG** for a hypoeutectic composition **2** on fig. 35. It is composed from primary phase **α,** crystallizing at a higher temperature, with a higher free energy value **ΔG,** corresponding to the point **2'** and eutectic **α+β** point **1**. Thus, for it the **ΔG** value becomes higher than for a purely eutectic composition **1**, even while in a traditional description alloys **1 и 2** are balanced out on the same line. Therefore, the heat capacity and free energy naturally in our approach depend from their melting temperature.

Now let's look more carefully at the phase equilibrium for compositions **1, 2 and 3,** containing eutectics below melting temperature (fig. 36).

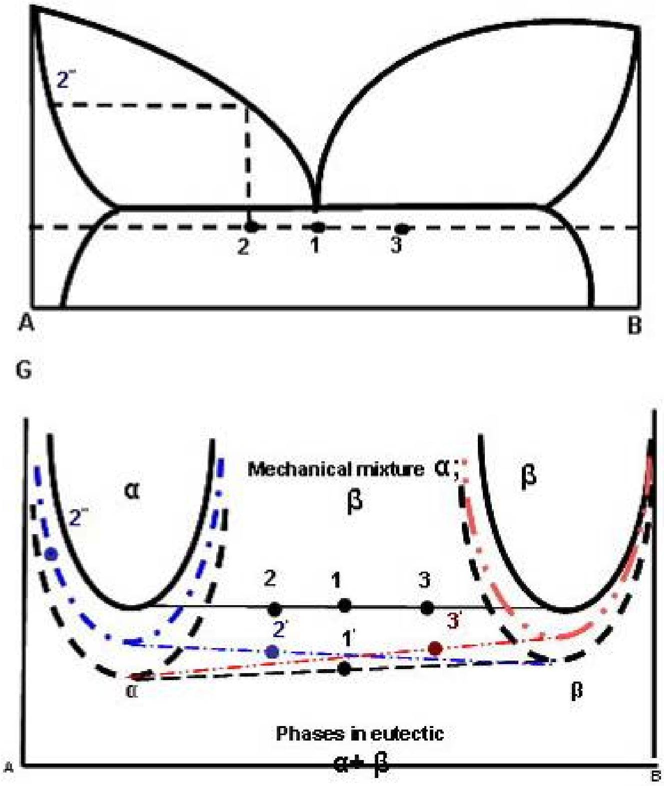


Fig. 36. Plotting free energy of mixing vs composition with account for interaction between phases using free energy curves ofr individual (not isolated) phases: *traditional description - (solid black line – average reduced value) – usage of free isolated phases in an alloy – phase equilibrium does not depend on alloy composition;*

*Proposed description according to the classical thermodynamics - (dotted lines) – usage of free energy from phases contacting with each other – phase equilibrium depends on composition (black – for composition **1**, blue – for composition **2** and red – for composition **3**) [7, 8]*

Alloys have the same phases **α** and **β,** but in different volume proportion. In the traditional description of phase equilibrium by a geometric thermodynamics method, when the mechanical phase mixture is taken as base (points **1, 2** and **3**), it is impossible to get eutectic alloy **1** from a preeutectic **2** and posteutectic **3**, because there are no free energy decreases (***solid black*** line on fig 4). But the real diffusion occurs anyway, because the free energy value decreases and should be represented by a *dotted* **black** *line* for composition **1**, *dotted* ***blue*** line for composition **2** and *dotted* ***red*** *line* for composition **3**. It is evident, that diffusion is possible at this approach, because the free energy of a forming alloy decreases (point 1**’** is lower than points **2’** and **3’**).

Therefore, unlike the mechanical description, where in multi-phase system the free energy value does not depend on the alloy composition, in a classical approach the free energy value does change because of the change in average heat capacity, like in solid and liquid solutions. *Naturally, there is a second pressing question – what is a physical mechanism of that change (which, naturally, has an energy context, like free energy) and how is it expressed on an interatomic bond level?*

Earlier [1], we have shown that any mixing causes strengthening of the interatomic bonds, due to valent electron levels splitting that fill newly formed levels converging. This additional bond is collective and it takes over the whole crystal volume. Swalin [5] writes: : “When foreign atoms are inserted into metal, an additional split of energy levels for valent occurs, as shown on fig 36, and the width of the strip increases. It does not mean the common chemical bond between nearby atoms, for example, **A** and **B**, which does not change its bond energy during ideal mixing. It means the additional collective interatomic bond, analogous to the metal bond in a crystal lattice. The valent electrons go to the lower levels, the atomic bond strengthens and the energy is released, ***compensating*** the increase of average heat capacity" *(fig. 37)*.

Cottrell creates a physical view of this collective connection: *«in a crystal, all atoms «feel» each other and every single atomic and energy level creates a quasi-continuous shelf of levels » [18].*

Therefore, Cottrell shows that this bond is applied to the whole crystal. This is our case of solid and liquid solutions. But it may be presumed that even in the heterogeneous structures the metal bond can transfer to the nearby phase, if the phases **are mutually oriented** to make a bond through the valent electrons level splitting, as will be shown in chapter 4.

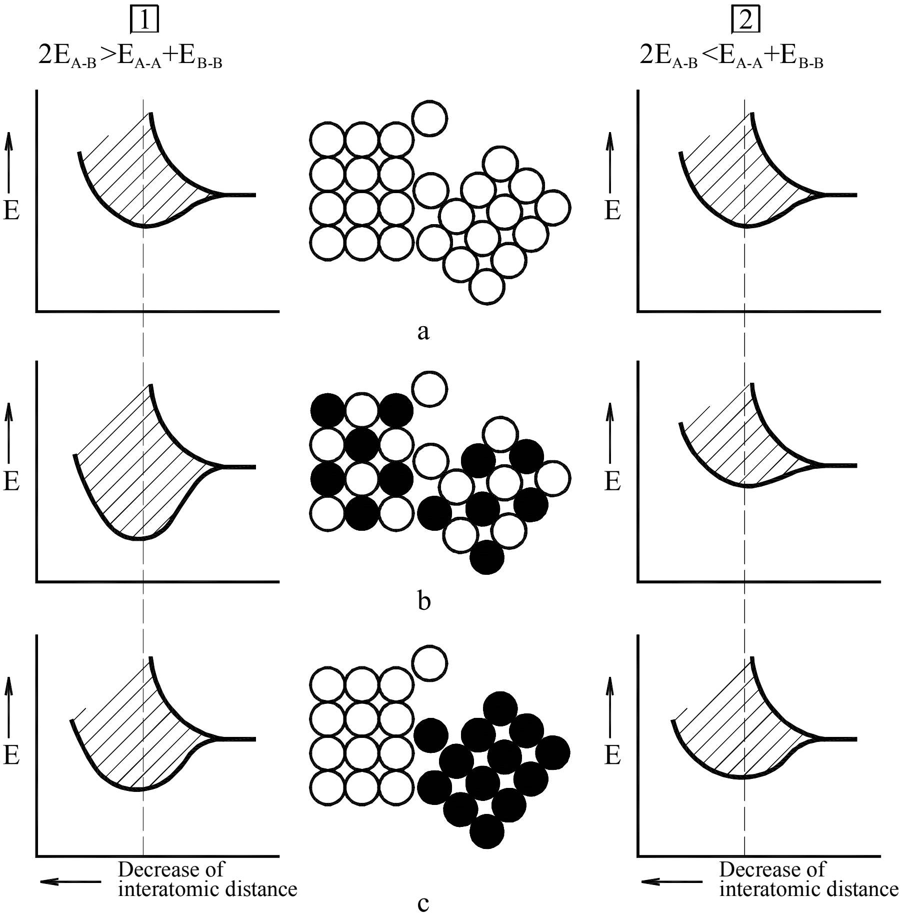


Fig. 37. Splitting of atomic levels (atoms A) of valent zone of electrons during the formation of: a) original isolated phases; b) melt; c) phases in eutectic [7-10, 19-22]

1 – alloys with negative energy of mixing ($2E_{A-B} > E_{A-A} + E_{B-B}$) and 2 – alloys with positive energy of mixing ($2E_{A-B} < E_{A-A} + E_{B-B}$)

This additional bond type, previously uncounted in alloys, can be nominally called **Interphase Metallic Bond** - IMB, a part of a common interatomic bond.

22. Experimental test of an interphase metallic bond in eutectics and the eutectic alloy melting mechanism

How is this bond expressed and could it be proven experimentally?

The interphase thermodynamic bond in alloys at the interatomic level reveals in the fact that despite the presence of individual phases **A** and **B** as well as the internal bonds **A-A** and **B-B** between those phases are available in alloys the A-B bond characteristic only of the liquid state as well as of solid solutions, is also partially retained. This additional bond is caused by an entropic contribution transforming in an additional interatomic bond strengthening and in a change in atomic oscillations nature, described in detail in [1, 2] and [20, 21, 27].

Therefore, it is expressed as a partial split of the electron levels corresponding to the **A-B** state. Since the **A-B** bond is a supplement to the **A-A** and **B-B** bond, the total amount of the interatomic bond increases which will lead to the lower energy level of valent electrons (fig. 37c) Thus, the atom **A** the phase **A** has bonds with both the adjacent atom **A** and the atom **B** available in the phase **B**. In its turn it might take place only upon the electronic interaction between **A** and **B** across the interphase boundary, i. e., until the specific mutual phase orientation is retained. If this orientation is upset the electronic interaction between the phases terminates, as a result the degeneration of electron levels will change and the melting temperature of an alloy will become equal to the melting temperature of initial components, Thus, an alloy turns into a common mechanical mixture of phases, as we have shown in our works [20, 21, 23-26]. We proved this hypothesis in a series of experiments on aluminum eutectic alloys.

It is known, alloys, particularly eutectic ones, are known to be easily overcooled by tens and hundreds of degrees below their melting temperatures without phase transformations taking place, however, so far they were never overheated even to one degree above their melting temperature even at high heating rates [28].

Currently, the lower alloy melting temperature (in comparison to the components melting temperatures) is explained by a mixing entropy increase in a liquid state, lowering the free energy of melting and stabilizing the liquid state in accordance with the second law of thermodynamics. Therefore, a high-energy liquid state of original components is preserved at crystallization. This is only thermodynamic model – even while there is no physical model and explanation of eutectic melting yet [16, 18].

In our works [1, 8] we have tried to show how mixing entropy energy does work, transforming into a vibrational entropy. A*verage heat capacity of alloys increases in mixing process due to a shift of heat capacity curves to the left – hence the decrease in Debye temperature – revealing that the mixing processes are accompanied by an increase of average heat capacity.*

The heat capacity theory from the point of molecular kinetic theory of atomic oscillations in a crystal lattice was developed by Debye and Einstein. According to their approach, heat capacity increases to the Debye temperature due to the increase in the frequency of atomic oscillations up to a maximum frequency ($\mathbf{v_{max}}$), specific to this metal crystal lattice. Heat capacity over the Debye temperature increases due to the increase in amplitude of atomic oscillations, becoming approximately 3R value. When oscillation amplitude reaches around 8-10%, according to the Lindeman's rule, the crystal lattice can't hold the thermal oscillations and destroys – the metal or alloy melts down.

While everything is more or less clear with the eutectic crystallization from a liquid phase/ *However, it is not quite clear how the reverse process i. e., the melting of eutectic alloy at a lower temperature proceeds.*

It is known, that during an eutectic crystallization from the molten mass with mixed atoms **A** and **B** and mostly interatomic bonds **A-B,** the crystals **AA** and **BB** are formed with **A-A** and **B-B**, bonds. How would these phases melt down at a lower eutectic temperature if there is no mixture of atoms, no **A-B** bond and, according to traditional thermodynamics, no mixing entropy? How does the phase mixture know that the time has come for it to melt down, and the melting is proceeding simultaneously at the same temperature throughout the whole bulk volume? The traditional thermodynamics of alloys does not give a clear answer to this question.

In order to explain this effect, it is assumed that an eutectic alloy is a mechanical blend of **AA** and **BB** phases and their melting starts along the phase boundaries where **A** and **B** atoms are in direct contacts. Then this inter-boundary zone has to immediately occupy the whole volume of an alloy. However, it has been experimentally establishes that eutectics both with fine and coarse grains that differ in areas of interphase surfaces by hundreds of time melt down throughout the whole volume without overheating at the same lower temperature although the heating rate reaches $\mathbf{10^6}$ deg/sec.

In order to check our hypothesis about the role of interphase metal bond commanding all eutectic phases to melt, seven aluminium based alloys were produced of the **Al-Si, Al-Cu, Al-Cu-Si, Al-Si-Ni, Al-Si-Ni-Fe, Al-Mg-Si-Cu, Al-Si-Mg-Cu** systems (table 1).

Table 1

Results of Measuring Melting Temperatures and Enthalpies of Al Base Eutectic Alloys [8-9]

N/N	Composition, % mass	Phase composition	Deformation degree, %	Melting temperature rise after deformation, ^0C	Decrease of enthalpy of melting after deformation, %
1	Al	Al	90	0	1.5
2	Al-11.5Si	Al+Si	90	4	11.2
3	Al-33Cu	$Al+CuAl_2$	4	9	8.1
4	Al-26Cu-5.2Si	$Al+CuAl_2+Si$	90	0	8.3
5	Al-11.8Si-5Ni	$Al+Si+NiAl_3$	90	3	10.1
6	Al-11Si-4Ni-1Fe	$Al+Si+NiAl_3+$ $(Fe,Ni)Al_9$	90	0	8.4
7	Al-9.2Mg-4.75Si-3Cu	$Al+Mg_2Si+Al_2Cu,Mg$	82	12	14.3
8	Al-14.3Si-5Mg-4Cu	$Al+Si+Al_4CuMg_5Si_{4+}$ $CuAl_2$	64	22	7.3

To decouple thermodynamic bonding the initial samples of the alloys were cold rolled at various deformation degrees. Upon rolling the phase orientation changed partially and at some sites the thermodynamic bond (internal metallic **A-B** bond between phases expressed by additional splitting of valent electron energy levels corresponding to the **A-B** state) was disturbed. However, metallography has not revealed any defects that lead to disturbance of metallurgical bonds between phases (fig. 38) [21, 23, 26, 27].

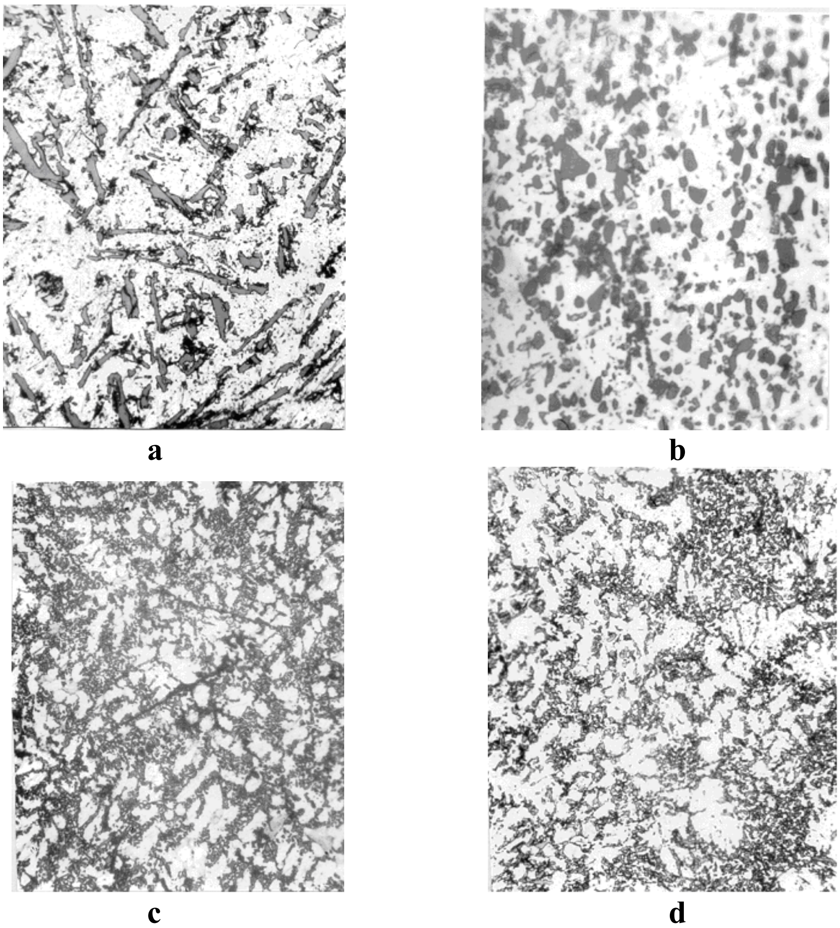


Fig. 38. Microstructure of Al-Si and Al-Si-Mg-Cu alloys prior and after rolling, a) Al-Si prior rolling, x420; b) Al-Si after rolling x1900; c) Al-Si-Mg-Cu prior rolling x420; d) Al-Si-Mg-Cu alloy after rolling x420 [21, 23, 26, 27]

The melting temperatures and enthalpies were determined by the differential thermal analysis (DTA) with BDTA-8M instrument in the helium environment after evacuation. Heating and cooling rates were 80 deg/min. Inside the instrument a thermostat made of pure tungsten was placed in the openings of which crucibles of 0.2 mm thick tantalum foil containing a sample and a tungsten standard were sited. The crucibles were connected directly to a W-Re thermocouple [11]. This instrument used to determine the temperatures of phase transformations in Pu and its alloys [12]. Therefore the accuracy of measurements was high (±1 ºC).

Experiment scheme is presented on fig. 39, its results – on fig. 40.

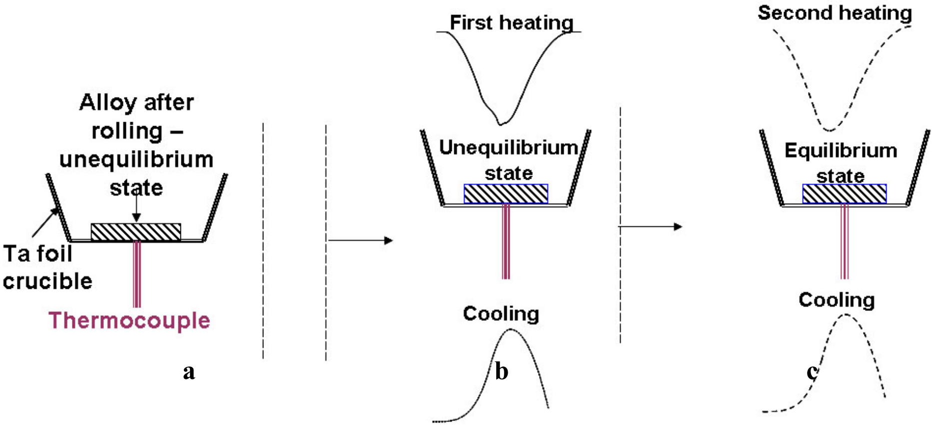


Fig. 39. Flow diagram of experimental procedure.

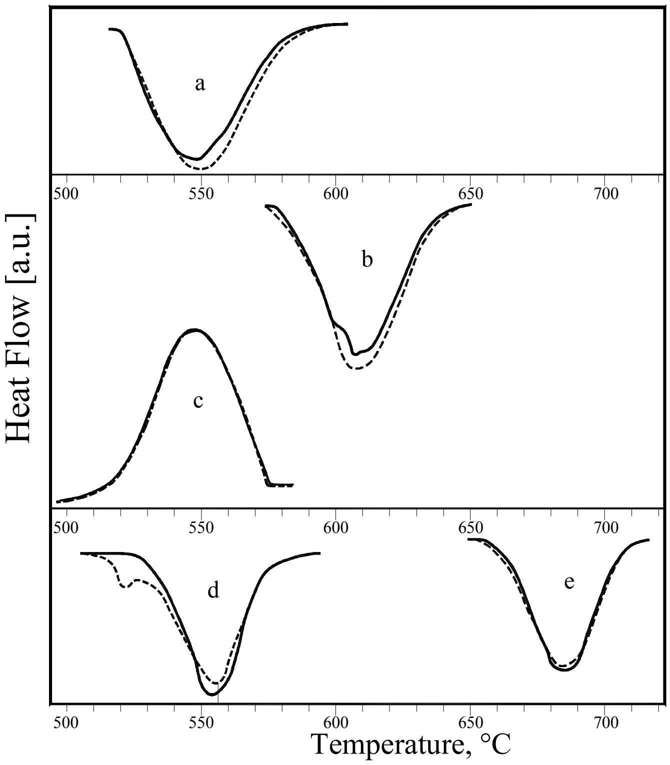


Fig. 40. Differential thermal analysis of the eutectic alloys: solid line - rolled samples (first heating), dotted line - remelted samples (original state - second heating), a) Al-Cu-Si - heating, b) Al-Si - heating, c) Al-Si - cooling, d) Al-Si-Mg-Cu - heating, e) Al – heating [21, 23, 26, 27]

In the DTA process the rolled Al-alloy sample with partly broken thermodynamic bonding was heated to melting (Fig 39. a, b and the solid line in fig. 40a, b, d). After melting the broken mutual orientation of phases was recovered and in this way the specimen restored its initial equilibrium structural state that it had before rolling. Then without removing from the instrument (fig. 39 c) the specimen having already the initial structure that it had prior to rolling with the recovered mutual orientation of phases and, hence, the initial equilibrium thermodynamic state (the dotted line in fig. 40 a, b, d - the condition of the original sample prior to rolling) was repeatedly subjected to DTA.

In this way the purity and accuracy of the experiment were attained since DTA was carried out on using the same sample but in another thermodynamic state. This procedure of testing allowed more accurate measurements of the differences in the temperatures of up to $\pm 1^0$C and the differences in the enthalpy of melting up to ±1%. This might be confirmed by the completely coincident cooling curves in DTA of rolled and original specimens since after melting down the alloys transformed into the equilibrium state (fig. 39b, c and fig. 40c). For the extra assessments of the error of the measurement method the same sample was heated for the third time. The third heating curves fully matched the second heating ones.

Melting temperature did not change in a control pure aluminum sample, melting enthalpy lowered only by 1.5 %, which is a deformation energy contribution (table 1, fig. 40e). The main change occurred in the beginning of meltdown, when there was a crystal lattice defects recombination.

In regards to aluminum eutectic alloy samples, the nature of their melting was significantly different.

There was a decrease of melting enthalpy after deformation, around 7-14 % depending on an alloy, numerically around 1 kilojoule/mole. This effect took place at the end of alloys melting., when there was a mixing process in a liquid state. First, at the eutectic melting temperature the undamaged by deformation part of eutectic melted down (fig. 40 arrow 1), while the phases that had been disoriented in the deformation process remained solid since after deformation their temperature of melting increased. With a further temperature rise their dissolution in the primary melt was attended with a release of the thermal energy of mixing (fig. 40 arrow 2), since they represented a simple mechanical blend of phases and were not a thermodynamically bonded part of eutectics. The breakaways (transitions) of the curves in figures 40b, 40d demonstrate the onset of this process. The energy release at mixing diminishes finally the enthalpy of melting. And this took place as it was pointed out above at the end of melting (fig. 40a, 40b).

For most alloys, the eutectic melting temperature increased as well, that is fundamentally novel result.(table 1, fig. 40).If the alloys had a strictly eutectic composition their temperature of melting became 3-9^{0}C higher (alloys 2, 3, 5), if they consisted of several eutectics (alloys 7, 8) their temperature of melting increased by 12-22^{0}C.

According to the presently available thermodynamic descriptions of eutectics as a mechanical blend of phases, the mutual phase orientation in eutectics does not influence on the melting process - either enthalpy or temperature of melting [16, 18]. However, this was not corroborated by our experiments.

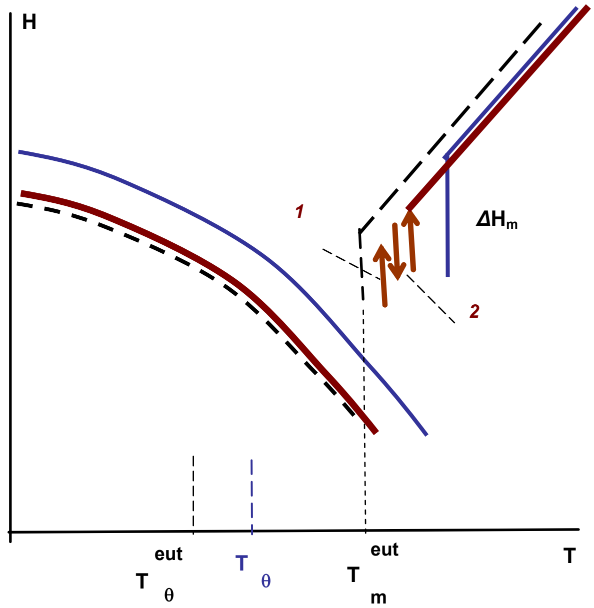


Fig. 41. Changes in enthalpy during heating eutectic alloy: dotted black line – re-melted samples (original state of eutectic - second heating); solid blue line – separate phases in eutectic (reduced average value - theoretical); solid red line - rolled samples (first heating) – thermodynamic bond is partly broken: arrow 1 – melting of undamaged part of eutectic, arrow 2 – heat release from mixing enthalpy

The received data on increasing melting temperature as well as change in melting enthalpy above the deformation energy of rolling contribution confirmed the statement that ***the thermodynamic state of alloys are changed.***

It was for the first time that the alloy was overheated above the melting temperature without a phase transformation at low heating rates (80 deg/min), proving our theory regarding the presence of an interphase metal bond in multiphase alloys. Due to the presence of this bonding eutectic alloys independent of their structure always melt down at the same temperature. Thermodynamic bond influences on the character and state of atomic oscillations, that results in lower melting points of eutectics.

Since this bond like the metallic one in metals manifests as splitting and extension of atomic energy levels of valence electrons and covers the whole depth of phases it may only exist at the specific mutual orientations of phases. Schematically, it is represented by long arrows on fig. 42 and remains during liquid-solid transformations and in reverse [1, 8].

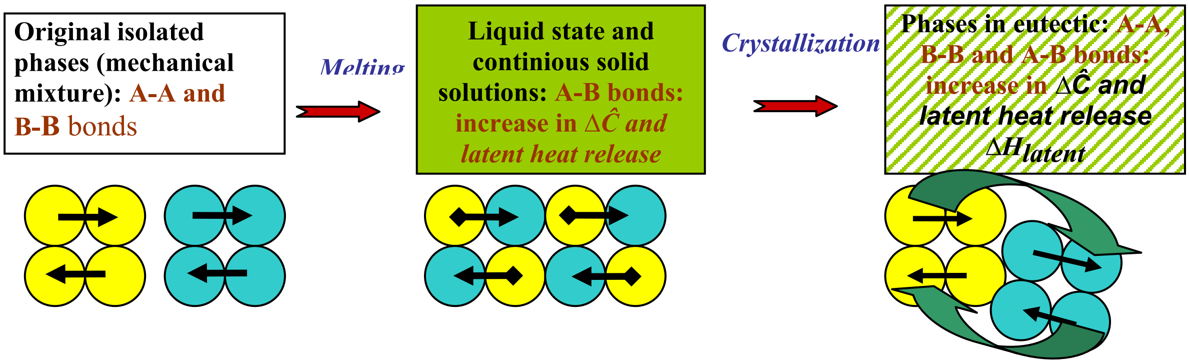


Fig. 42. Schematic presentation of thermodynamic bond formation in eutectic alloy

From this position, we can explain the «depressed melting» phenomenon - when metal melts down at lower temperatures. Surface energy causes the disorder and entropy to rise and transforms into a oscillation mode increase (determined experimentally), shifting the Debye temperature to the left and lowering the melting temperature. These are, again, the hidden effects of increasing average heat capacity and entropy revealing at various impact on materials.

23. Thermodynamic description of a phase equilibrium and evaluation of interphase metallic bond value in multiphase alloys.

In the preceding chapter, we have reviewed the multiphase systems forming simple eutectics, which mostly have a weaker bonds in unlike atoms than in tha same atoms. But most alloys are systems with intermetallic compounds (fig. 43).

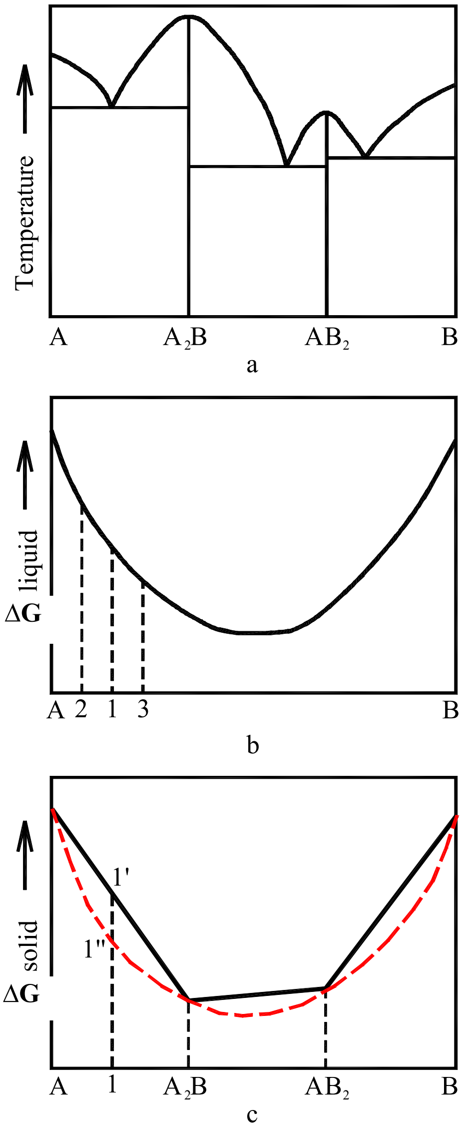


Fig. 43. Free energy of mixing as a function of composition and corresponding to it phase diagram with intermediate phase; a) Hypothetic eutectic phase diagram with intermediate phases; b) Energy of alloy mixing vs composition in liquid state; c) Energy (enthalpy) of alloy formation vs composition in solid state; straight line – traditional thermodynamic description that describes the mechanical phase mixture; dotted line – actual alloy state as a single thermodynamic system.

For simplicity reasons, the complex state diagrams are usually separated into simple ones, and intermetallic phases are considered as individual chemical components. Thus, all noted regularities of thermodynamic description of interphase metallic bond energy and change in thermodynamics parameters of the system, stay in power. But we should note, that the intermetallic phase, unlike the pure component, is a mixture of **A** and **B** atoms, even structured in a solid state. Therefore, as in solid and liquid solutions, their mixing entropy energy put into them, expressed as an average heat capacity increase, and strengthening of interatomic bonds. But due to a dominating contribution of the nearby unlike atoms bonds **A-B,** the entropy contribution is hardly noticeable in intermetallic compounds. But it is tangible at higher temperatures (Δ**ĈT**), that's why intermetallics retain their high mechanical properties up to a melting temperature and complex chemical intermetallic compounds (more than 5 components) have increased thermodynamic stability/ .

As was explained in chapter 3 in the description of thermodynamic equilibrium of simple eutectics, one has not to use the values of the free energies of isolated phases as it is practiced currently but to use the free energies of the same phases contacting one another. As distinct from isolated phases, the value of the free energies of individual phases in a mixture shall be lower, and the free energy curves of the individual phases in the alloy of the particular composition shall be below (fig. 44). Then the condition presently accepted in the thermodynamics of alloys might be retained when the free energy of the particular phase mixture will be equal to the mean free energy of individual (but not isolated) phase, in other word $\mathbf{F_{sp1}=F_{\alpha1}+F_{\beta1}}$ for composition **1** (*the red lines in fig. 44)* and $\mathbf{F_{sp2}=F_{\alpha2}+F_{\beta2}}$, for composition **2** (*the blue lines in fig. 44)* and its value will be determined by the location of the point that corresponds to the alloy composition on the straight line connecting the points the location of which is determined by the free energy value of individual (not isolated) phases (fig. 44) [20, 21].

a

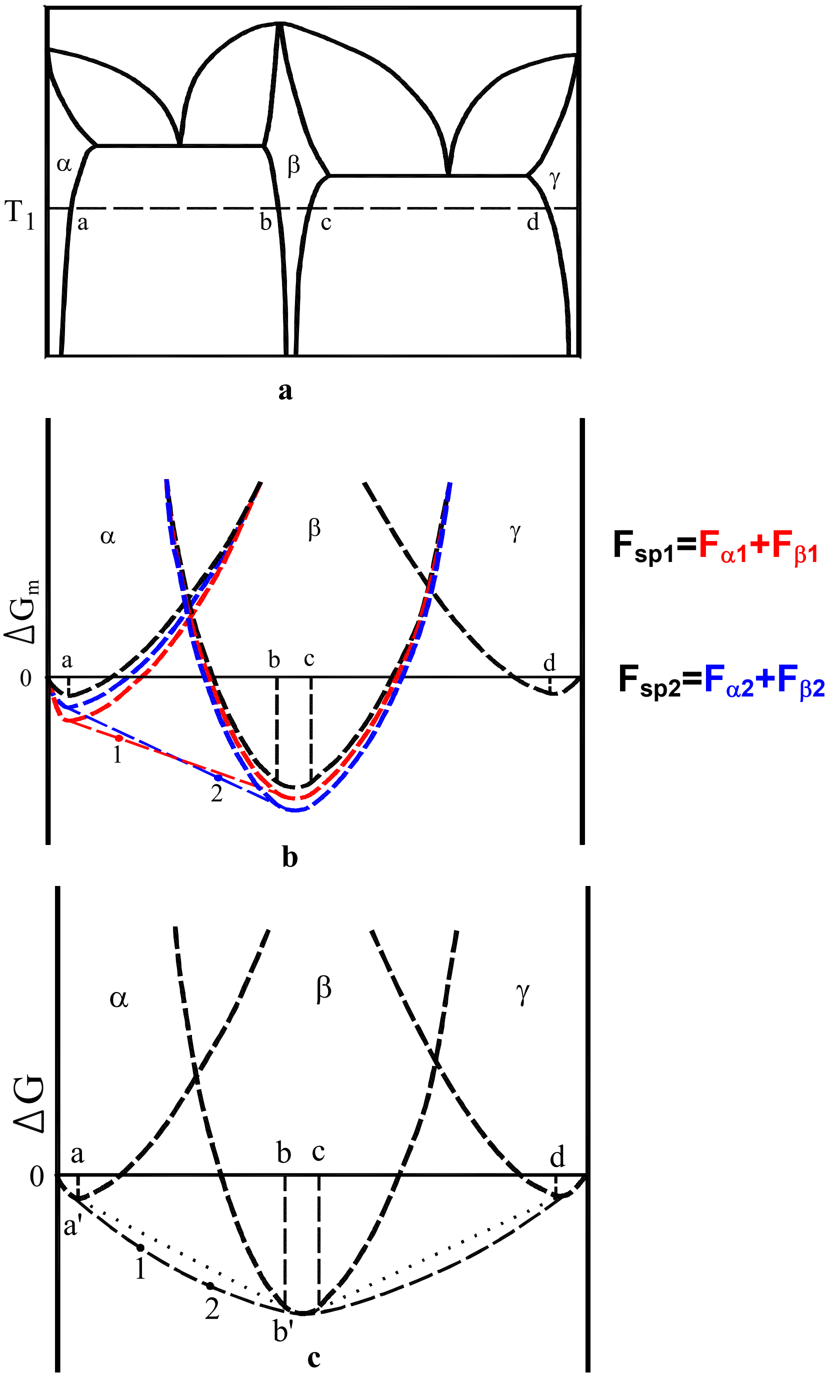


*Fig. 44. Plotting free energy of mixing vs composition with account for interaction between phases using free energy curves for individual (not isolated) phases for phase diagram with intermediate phase: black colour – isolated phases, red colour – alloy of composition **1**, blue colour – alloy of composition **2**.*

***(в) dotted line** – isolated phases, **dashed line** – alloy phases [20, 21]*

As distinct from the conventional description at the particular temperature the value of the alloy free energy shall be dependent on the alloy composition, i.e., the quantitative phase ratio in an alloy. This complicates the free energy curve construction by the geometrical thermodynamics methods throughout the range of composition.

That is why, ***to facilitate the description*** of the phase equilibrium using the free energy curves it is also possible as in the traditional thermodynamics to proceed from the curves of the free energies of isolated phases and to present the free energy of the phase mixture depending on the composition not by the tangent line but by the parabolic curve (fig. 45c). The difference between the curve and the tangent to the free energies of isolated phases shall correspond the value of the thermodynamic bond and distinguish the alloy from the mechanical mixture of phases.

The interphase thermodynamic bond in alloys exists not only between the phases of an eutectic alloy but also between the primarily crystallized phases and the eutectics (fig. 45) [20, 21]. Consider a part of the phase diagram (fig. 44) between the **A** and **A_2B** phases and reduce to zero the values of the alloy formation for the **A** and **A_2B** phases (fig. 45). Let’s take the alloy composition **2** the formation energy of which corresponds to the point **2□**. The alloy structure consists of two structural components: primary crystals **A** having the alloy formation energy equal to zero (point **1**) and the **A+A_2B** eutectics of the compositions **4**, with the formation energy of which equals **4□-4□**.

Part of a state diagrams **A-A_2B** with eutectics and phase bond energy expressed via energy of alloy formation (relative values of the alloy formation energy for **A** and **A_2B** phases are reduced to zero).

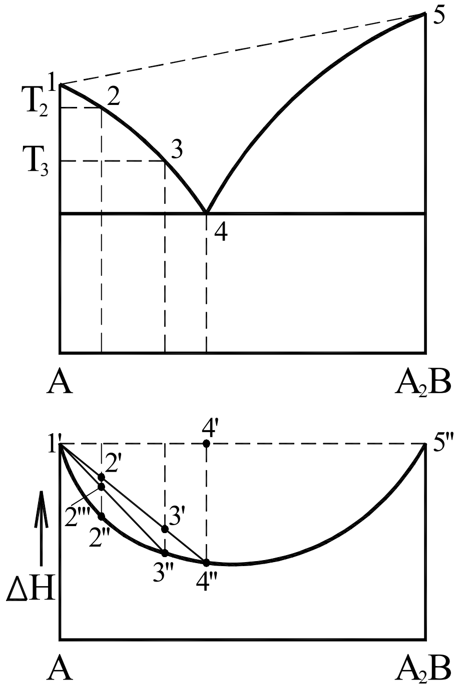


*Fig. 45. Phase diagram part **A**- **A_2B** with eutectics and phase bond energy expressed via energy of alloy formation (relative values of the alloy formation energy for **A** and **A_2B** phases are reduced to zero)*

Hence, for alloy **2** the average sum of those energies is at the point **2□** that is on the straight line connecting points **1□** and **4□**, in other words, this energy corresponds to the mechanical mixture of the initial structural components of alloy **2**, the primary phase **A** and eutectics **A+A_2B.**

As is shown by fig. 45 this value of the energy (of the mechanical mixture) is somewhat lower than the energy of alloy **2** formation. That is why, it is the difference between the energies equaling **2'-2"** is the mean energy of the bond of the primary crystal phases **A** with eutectics **A+A_2B**. If it is desired to have the absolute value of the energy it is to be reduced to the mole fraction of the primarily released phase.

Interphase thermodynamic bond has to exist not only between the primary phase and the eutectics, but also between the primary phase and molten mass. At this the primary phases crystallized at higher temperatures have weaker energy connection with retained melt than following primary phases at lower temperatures.

When there is an eutectic state diagram with some limited solubility in a solid state, then the crystallization of alloy **2**, a solid solution would be released first instead of a pure component **A** (point **3** on fig. 46). Thus, when the pure component has zero formation energy, for a solid solution at temperature **T_2** energy formation corresponds to a point **3"**, and at further crystallization increases to point **5"**.

The thermodynamic bond has to exist also between the primary phase and the molten mass as well as between the molten regions that offer in their compositions and structures. It is most likely that it is also inherent in not only metal likely systems but also in different types of liquid solutions where fluctuations, non-uniformities and clusters are feasible.

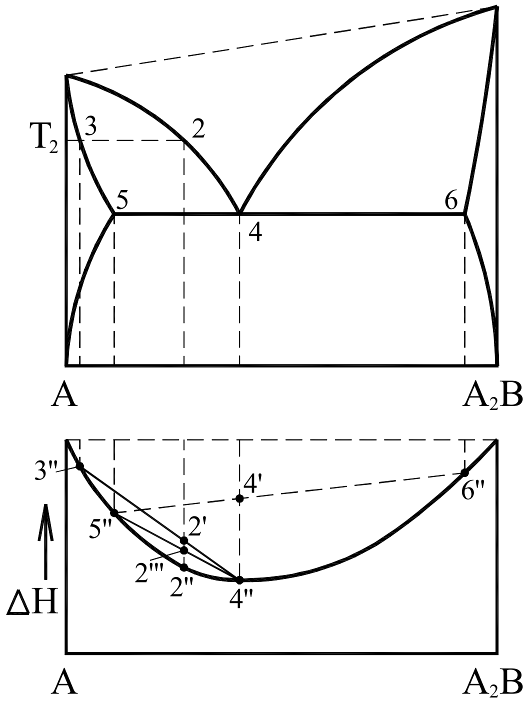


*Fig. 46. Phase diagram part **A**- **A_2B** with eutectics (and limited solubility in solid state) and phase bond energy expressed via energy of alloy formation (relative values of the alloy formation energy for **A** and **A_2B** phases are reduced to zero)*

Therefore, because a part of mixing energy is already spent on forming the solid solution based on the component **A**, its bonding energy with eutectic would be somewhat lower than for a dissolution-free system in a solid state at the same energy formation value. For a solid solution of composition **3** it is equal to **2′-2″**, for composition **5** in a point of maximum solubility – to **2″-2‴** value. Therefore, the phase bonding energy at eutectic temperature would be equal to **4′-4″**, i.e. lower than for a phase solubility-free system, with equal formation energy.

The geometric method for evaluating the interphase metallic bond provides a clearer picture.

More accurate method - the "heat balance" one – allows to get accurate numerical values, but in calculations many thermodynamic parameters should be considered, such as heat capacity of original phases in liquid and solid states, their dependence on temperature, temperature and enthalpy of melting of alloys and constituted alloy phases, as well as mixing energy in a liquid state.

In this method, comparison is made of the energy spent to heat up to the liquid state until the specific temperature is reached (e.g., from the temperature of the eutectics melting to the melting temperature of the higher melting phase A) of the eutectic alloy itself and its phases with account for the energy of mixing, the difference between them is the energy of the interphase metallic bond.

The principle itself is provided in the works [20, 21]. Thus, for the eutectic composition alloy this equation has the general form of:

$$E_{xA+yB} = x \cdot C_A^S \cdot (T_A^m - T_E^m) + x \cdot H_A^m + y \cdot C_B^S \cdot (T_B^m - T_E^m) + Y \cdot H_B^m + y \cdot C_B^L \cdot (T_A^m - T_B^m) -$$

$$- E^{mixed} - (x+y) \cdot H_E^m - (x+y) \cdot C_E^L \cdot (T_A^m - T_E^m),$$

where E_{xA+yB} is energy of interphase thermodynamic bond in eutectics,

T_A^m, T_B^m, T_E^m are melting temperatures of A, B phases and the eutectics, respectively,

C_A^S, C_B^S are heat capacities of A, B phases in the solid state,

C_B^L, C_E^L are heat capacities of phase A and eutectics in the liquid state,

H_A^m, H_B^m, H_E^m are enthalpies of A, B phases and the eutectics melting, respectively,

E^{mixed} is energy of mixing of A and B phases in the liquid state,

x, y are mole fractions of A and B phases in eutectics.

The calculation has to take into account a variation of the heat capacity vs temperature. To calculate the formation energies of hypo- and hypereutectic alloys the heat balance is made up with account for the primarily crystallized phases.

We can also use a purely thermodynamic calculation, with liquidus and solidus curves and standard thermodynamic values – melting entropies and enthalpies. But formulas proposed by this method are only approximate and half-empiric [20, 21].

24. The influence of interphase metallic bond on alloy properties

The interphase metallic bond is one of the earlier unknown varieties of the interatomic bonds existing in both solid and solid-liquid states, therefore it affects physical, chemical and mechanical properties of alloys.

The general schema of the influence exerted by the interphase metallic bond on the alloy properties is illustrated in fig. 47 [20, 21].

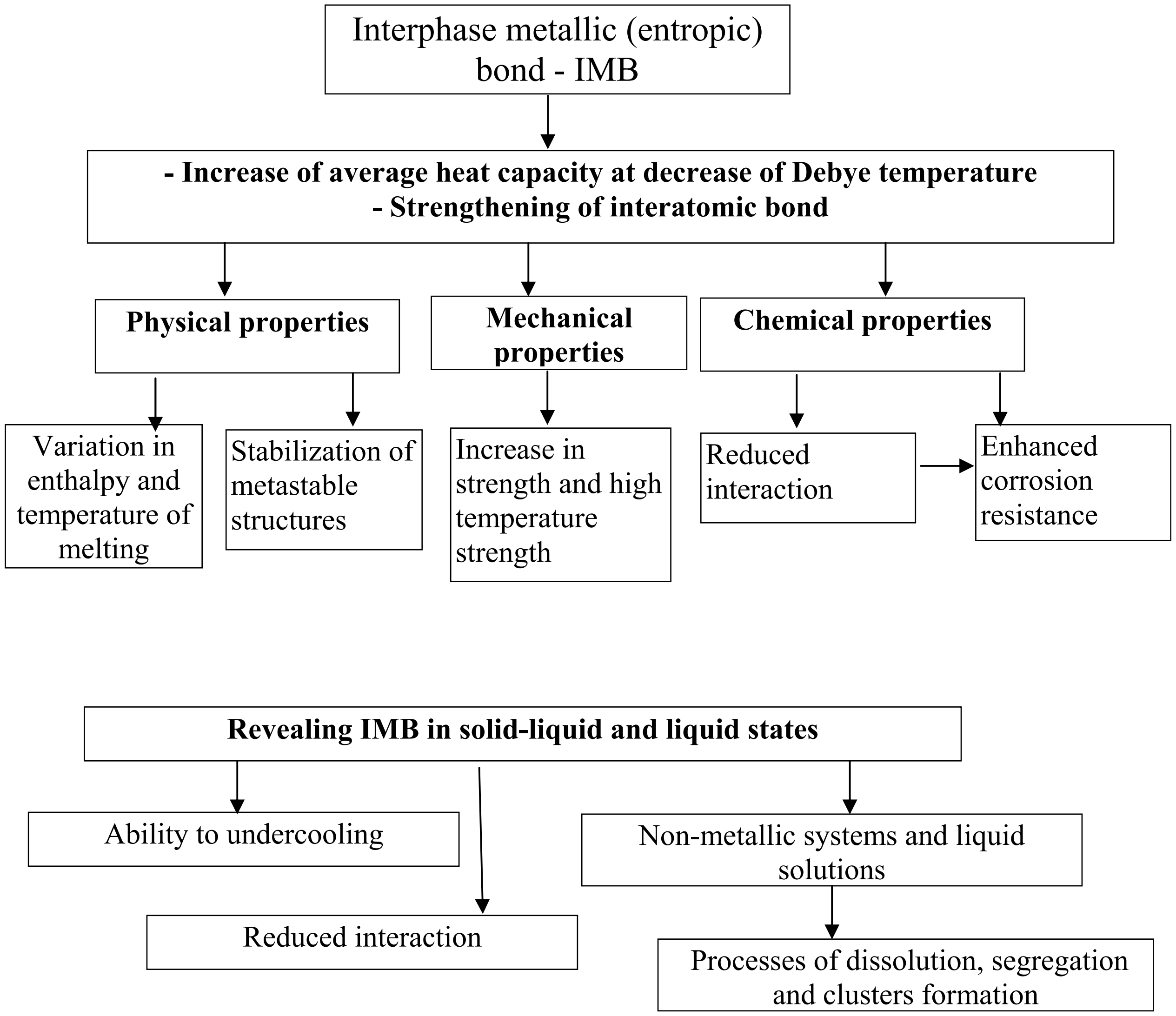


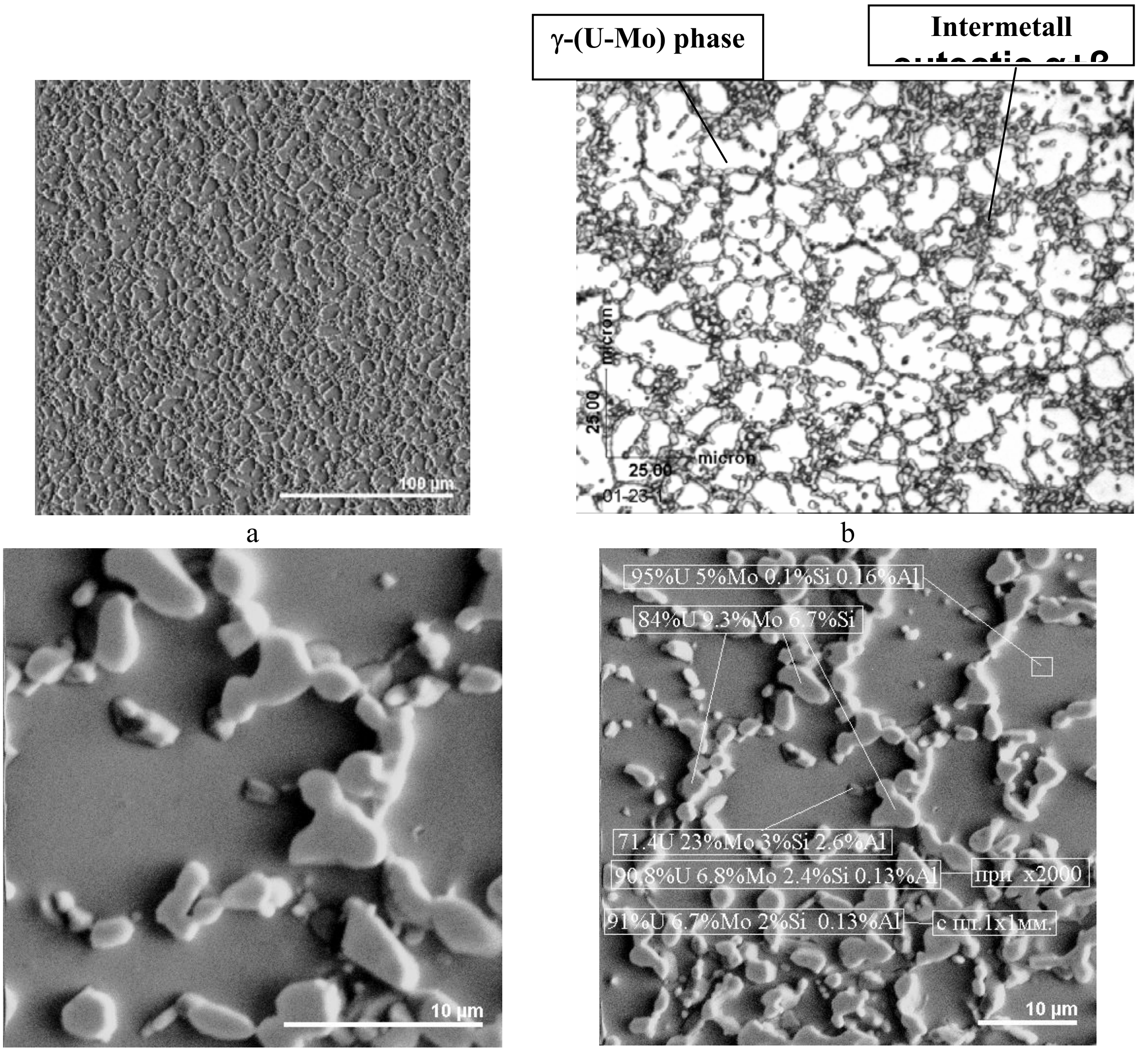
Fig. 47. Influence of interphase metallic bond on properties of alloys [20, 21]

The main affecting on alloys properties factors are the increase of average heat capacity due to the decrease of the Debye temperature **(T^Q)** and the strengthening of an interatomic bonds (formation of a interphase metal (entropic) bond **(IMB)** in an multiphase system).

In chapter 4 we showed that these effects influence the temperature and enthalpy of melting in an eutectic, where these effects are most pronounced, as well as in the other heterogeneous alloys. That is why aside from the ability of determining the eutectic point from the magnitude of the interphase thermodynamic bond and, hence, its use to calculate phase diagrams one can understand the causes of alloys melting and via acting on the bond vary the melting temperature of alloys, which was achieved on Al-Si-Mg alloy [21, 26, 27].

The interphase thermodynamic bond shows up primarily in the stronger interatomic bond that is why, it influences the strength and high-temperature strength of alloys. For instance, the stronger interatomic bond in the main matrix phase of the alloy at the expense of the bond to the atoms of alloying elements that are available in the adjacent strengthening phases and do not enter the solid solution of the matrix-phase leads to an increase in the strength of the alloy as well as high temperature strength. However, it has to be taken into account that at temperatures above 0.7 of T_m of the matrix the high strength properties become lower because the melting temperature of the strengthening phase is lowered down due to its thermodynamic bond with the matrix phase. Therefore, at those temperatures either alloys having the minimal interphase thermodynamic bond have to be used or this bond has to be broken by different ways to obtain a structure of the mechanical mixture type. The analogous of those alloys might be high temperature strength composites produced by powder metallurgy methods (mechanical alloying) that retain their high temperature strength up to 0.9 T_m of the matrix.

The effect described above – influence on the stability of the main phase by the elements in the other phase through the mutual grain boundary - was discovered during the development of new uranium alloys for high-density fuels in accordance with The Reduced Enrichment for Research and Test Reactors program (RERTR). We have developed an alloying concept for gamma-phase uranium alloys, in particular, U-Mo fuel – formation of a double-phase alloy structure, comprised of a main γ-(U-Mo) phase and intermetallic or ceramic type phase, precipitates on grain boundaries [29, 30]. First tests have proven the viability of this direction (fig. 48).



a b

c d

Fig. 48 Structure of an alloyed UMo double-phase alloy, a, b – U+5,7Mo+0,9Si; c, d - U+6,3Mo+0,9Si+0,15Al

The main difficulty in alloying γ-U phase alloys, for example, U-Mo fuel, lies in the reduction of γ-(U-Mo) phase stability due to the decrease of molybdenum content when alloying elements are added, particularly Al and Si. Some amount of molybdenum from gamma-uranium phase is included in intermetallic phase, therefore, weakening the gamma phase solid solution by Mo. This should reduce its stability.

But in our case γ-(U-Mo) phase stabilization occurred at relatively low concentration of Mo in gamma-uranium phase. This effect can be explained by stabilizing acting of elements at the second phase through their mutual grain boundary [8, 21, 24]. This is very interesting effect, confirming our approaches of existing IMB in multiphase systems, opens the possibility of γ-phase stabilization using limited quantities of alloying elements and refers to fundamental aspects of metal science.

To develop heterogeneous alloys having high electrical conductivity and strength their structure has to be a fully decomposed solid solution (at the minimal solubility of alloying elements) strengthened with intermetallic phases. In this case it was not taken into account that the alloying elements that form the composition of intermetallic phases might be significantly thermodynamically bonded to the solid solution. While not directly entering the solid solution the atoms of alloying elements available in the intermetallic phases at the level of the valent electrons due to the thermodynamic bond are as if they were in a solid solution, thus, additionally reducing the electrical conductivity of the alloys. Therefore, the disturbance of this bond by deformation (drawing and rolling) though it may seem paradoxical, has to lead to an increase in the electrical conductivity. This takes place, e.g., in carbon steels where the effect of the increased electrical conductivity after rolling has not found a scientific explanation. Therefore this effect has to be taken into account in development technologic methods and alloys of high electrical conductivity.When studying the chemical interaction of various materials in a solid state we should consider, that when a strong interphase metal connection is formed, the other interactions weaken, i.e. the compatibility improves.

When investigating the chemical interaction between different materials in a solid state one has to account for that in case a strong thermodynamic bond is formed the interaction with other materials decreases, i.e., the compatibility between the materials improves. This takes place at the expense of a lower energy condition of an alloy as compared to that of the mechanical blend of the phases.

One of the versions of the chemical interaction is corrosion and the interphase surface metal – metal oxide with the specific mutual phase orientation might be considered to be a system with a thermodynamic bond. In the majority of commercial alloys, particularly on Zr and Fe base, after a certain period of uniform corrosion the stage of an accelerated corrosion begins that results in a quick fracture of the metal. While studying the corrosion behavior of zirconium we have advanced the hypothesis that this process takes place due to a disturbance of the thermodynamic bond at the boundary between the metal and the oxide [20]. The availability of this bond decreases the system energy and slows down the material-environment interaction. Proceeding from this concept it is explainable the phenomenon of the amorphization of fine intermetallic phases in the oxide films and zirconium itself under in-pile irradiation.

Interphase metal bond also exists between the original phase and the melt, for example, in the development of so-called Accident Tolerant Fuel, resistant to the emergency situations [30-33]. In order to low down the temperature in the center of a fuel element and to improve the economical characteristics of a reactor therewith increasing of uranium concentration, a transfer is proposed from dioxide fuel to disilicide uranium U_3Si_2, with uranium capacity 17% higher. At the same time, for 50% more dense silicide U_3Si fuel is not considered due to its low solidus temperature [33-35]. Main reason – its liquid-solid state in emergency situations (at 1100 ^{0}C) according to the phase state diagram (fig. 49). With that, according to the traditional thermodynamics, whish consider any alloy as a mechanical mixture of phases, the liquid part of uranium melt would eat the zirconium cladding of a fuel element, and the fuel would pour down. According to our approach, the interphase bond will not allow these processes to happen, as was experimentally proven by heating the RBMK type fuel element sample with U_3Si fuel at 1150^{0}C for 30 minutes as imitation of accidents [36-38]. The sample retained its form and dimensions. The inner-diffusion zone was only 30 microns (fig. 50).

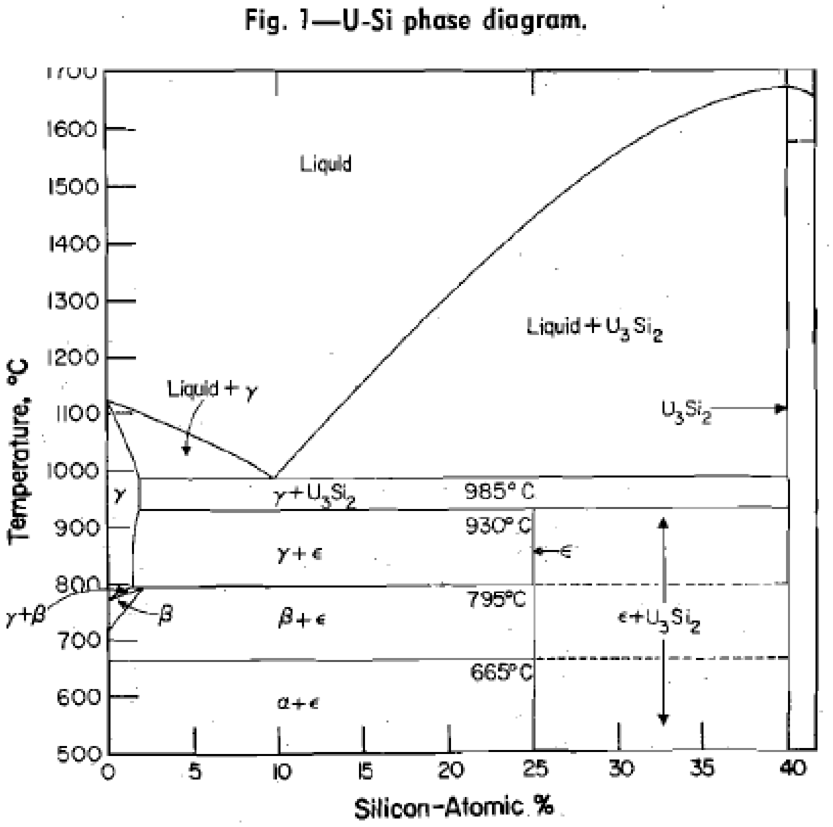


Fig. 49. State diagram U-Si with explored U_3Si fuel area

Therefore, we can implement a denser U_3Si fuel as tolerant fuel instead of currently used U_3Si_2 or intermediate U_3Si- U_3Si_2 composition. Additionally, the emergency scenario will be facilitated, because the cold fuel lowers down the fuel temperature.

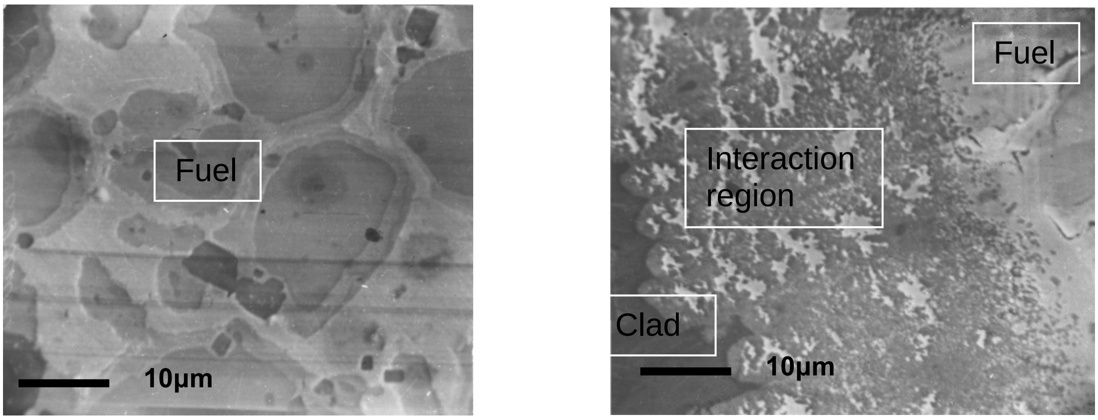


Fig. 50. Silicide fuel element structure after emergency test (1150^0C for 30 minutes) [36-38]

The interphase thermodynamic bond has to show up in the especially strong way in nanostructures where the interphase surface is large. Presently these materials because of their unique properties are used in various fields of engineering. The knowledge of the specific features inherent in the formation and the physical nature of this bond might allow the improvement of the properties of this class of materials.

The thermodynamic bond has to exist also between the primary phase and the molten mass as well as between the molten regions that offer in their compositions and structures. It is most likely that it is also inherent in not only metal likely systems but also in different types of liquid solutions where fluctuations, non-uniformities and clusters are feasible. One of the systems of this type is blood having different bodies, antibodies and viruses and etc.

One has to keep in mind that that the interphase metallic bond is inherent in all types of alloys, not only in eutectic ones. However, its maximal magnitude and, hence, the maximal effect on the properties of alloys reveals particularly in the systems of the eutectic type. It is especially pronounced in deep eutectics as well as in compositions with melting temperatures much lower than the line of reduced temperatures.

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25. Conclusion

1. Shown that at crystallization, where the homogenous mixture separates into heterogeneous solid phases, the energy content of mixing entropy does not disappear but transforms into vibration entropy. This effect, just like in solid solutions, causes an increase of the average heat capacity and simultaneous strengthening of interatomic bond energy.
2. As a result a mismatch is discovered between the thermodynamic description of alloys as a mechanical phase mixture and their actual state as a unified thermodynamic system, where an intricate physical and chemical interaction between phases is observable. Hence, for describing the thermodynamic state of alloys it is suggested in place of the presently adopted values of isolated phase free energies to use the free energies of the same phases contacting one other. As a result, the free energy of an alloy is reduced.
3. Therefore, the average heat capacity values of the phases comprising a multiphase alloy or eutectics become higher than in the original isolated phases. Hence, considering thermodynamic phase equilibrium and following Gibbs interpretation, dependence of the free energy values of mixed separate isolated phases versus composition shall be not-linear as it is presently assumed but a parabolic one as for solid and liquid solutions.
4. This bond between phases akin to a metallic bond, *where valent electrons of one phase interact with the valent electrons of another eutectic phase through mutually oriented interphase borders. As a result, the atomic fluctuation nature changes, the Debye temperature lowers, causing the melting temperature to lower as well. As a result, the free energy value of the system decreases.*
5. Phases in eutectics additionally forms internal bonds that distinguish alloy from a mechanical blend of phases. This bond can arbitrarily be called an interphase metallic one. The interphase metallic bond in alloys at the interatomic level shows up in the fact that despite the existence of individual phases A and B and internal bonds A-A and B-B in the structures of alloys these phases partially also retain the A-B bond that is only characteristic of a liquid state. This bond reveals as the partial splitting of the electron levels that corresponds to the A-B state and exists until the specific mutual phase orientation is retained. Therefore, valent electrons of one phase can interact with the valent electrons of another eutectic phase though mutually oriented interphase borders. As a result, the atomic oscillations nature changes, the Debye temperature for eutectic alloys becomes lower that make them melts at lower temperatures simultaneously in the whole alloy.
6. Preliminary tests on various aluminum eutectic alloys proved this hypothesis. By changing the mutual orientation of phases we managed to overheat the alloy by 22 degrees Celsius over the melting temperature without a phase change at a low heating speed (80 degrees/min).
7. The interphase metallic bond is one of the previously unknown varieties of interatomic bonds that exists between phases both in solid and solid-liquid states, that is why, it influences many properties of alloys. As forming alloy (particularly eutectic one) we observe changes in free energy, entropy, heat capacity and hence – in character and energy of atomic oscillations. Therefore, it affects: temperature and enthalpy of melting, heat capacity, coefficient of thermal expansion,

strength and high temperature strength as well as diffusion processes, that in turn influences on compatibility, corrosion, material performance, etc

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